

NOTES ON CHEMICAL ANALYSIS

BY

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PREFACE

It is impossible to write a completely comprehensive text-book of analytical chemistry, on account of the infinite variety of conditions governing different chemists in different kinds of work. Every chemist makes his own selection of methods for his special uses from all the literature that he knows. He depends on his own experience so far as possible in judging methods; and when that fails, prefers methods that are written by specialists from their experience. He avoids the methods which plainly have been "only writ for filling, to raise the volume's price a shilling."

The writer, therefore, makes no apology for the fragmentary character of this book. It is a collection of things which he believes to be worth recording, and which have been verified by his own experience. He hopes that other analysts may find some of his suggestions valuable.

CONTENTS

	PAGES
CHAPTER I.	
Glass-working. Apparatus and Tools. Balance and Weights. Calibration of Glass Apparatus. Table of Corrections for Glass.	1-33
CHAPTER II.	
Tabulation Method for Chemical Calculations. Problems. Cor- rection for Metallics in Ore Assay.....	34-40
CHAPTER III.	
Some Properties of the Commoner Elements.....	41-62
CHAPTER IV.	
Reagents, Properties and Uses.....	63-70
CHAPTER V.	
Fundamental Operations. Filtering and Washing, Destroying Organic Matter, Evaporation. Methods of Decomposition. Alloys. Ores, Acid Treatment. Fusion Methods.....	71-86
CHAPTER VI.	
Qualitative Analysis. General Scheme.....	87-109
CHAPTER VII.	
Determinations.	110-128
CHAPTER VIII.	
Separations. Tin, Antimony and Arsenic. Copper Separations. Lead Separations. Bismuth Separations. Cadmium and Zinc. Bronze. Aluminium Separations. Uranium Separations.	129-155

CHAPTER I

GLASS-WORKING

Glassware undergoes surface deterioration with age and use. This causes roughening, and often cracking, when the glass is heated. If the part to be worked is soaked for a minute in a mixture of one part HF solution and about ten parts water, rinsed in distilled water and dried, it may be softened and welded as easily as new glass.*

The art of glass-blowing consists largely in the ability to hold the parts steadily in the flame and to apply the heat equally all around. A little practice on scrap tubing, holding one piece in each hand and turning it in the fingers or with the wrist, half way around, or a trifle more, and back, about two turns to the second, will help to give the steadiness necessary for welding.

Bulbs.—The tube should be heated until the end closes, then removed from the flame and blown. When blown in the flame, the thinnest part gives way most, and soon breaks into a hole. When removed before blowing, the thinnest part becomes hard first, while the thicker parts continue to expand. If a large bulb is desired, the first small bulb should be heated to thicken it and the tube heated farther back and blown, so that more glass is included in the bulb. This process may be repeated until enough glass has been brought into the bulb. It is then reheated and blown slightly until the glass is evenly distributed, and then blown to its final size. The turning should continue as long as the glass is soft.

Thistle Tube.—Make a bulb, soften the end of it and burst it by blowing suddenly. Crush off the thin edge of the rim thus formed and thicken it in the flame.

Side Hole.—Close one end of the tube with a rubber plug or by fusion. Direct a small jet against one spot, while blowing gently, until an expansion appears. If a pin hole is required, turn the tube so that the flame blows across, not against, the top of the expansion, and keep on blowing gently until a break occurs. For a larger hole, soften a larger spot, remove it from the

* "The Devitrification of Glass." A. F. O. Germann, *J. A. C. S.*, Jan., 1921.

flame and blow quickly, as in making a thistle tube. Thicken the edges in the flame and correct the shape, if necessary, with the molding tool.

Molding Tool.—Grind a stick of arc light carbon to a fine conical point. It may be used to alter the shape of open ends and edges. Hot glass will not stick to it as it does to hot iron or platinum.

Welding Tubes.—The ends of the tubes should be cut off square. They should be as nearly as possible of the same composition, so that they will have the same rate of expansion and will not crack on cooling. If they are not the same size, take the larger piece and roughly weld a short piece of rod or tube to it. Heat the tube at least half an inch away from the joint, so that the contraction will be round, and draw it down to the proper size and thickness of wall. The less the glass is pulled in proportion to the time and intensity of heating, the thicker the walls will be. Cool the piece, scratch it with the glass knife or file, and pull with a very light bending stress to crack it off square. Ordinarily, if the file or glass knife is sharp, the break will be square. If it is not, lay the end on a board with the longer side up and crush chips off the edge by bearing down on points near the edge with the file or knife.

Now close all the holes but one of the pieces to be welded, except the ends to be joined. If any delicate parts, such as stop-cocks, are within two inches of the heat, protect them with sheet asbestos or cloth. Fasten a flexible rubber tube about two feet long to the extra hole, and hold the end of the tube in the mouth. A short piece of glass tube at the end covered with the rubber tube makes a good mouth-piece. The extra hole should if possible be in the axis of the weld or parallel to it.

Using a small flame, heat the two ends until they are soft at the edges only. Bring them together as accurately as possible, advancing them as little as possible to make an air-tight joint. The two pieces should be turned back and forth in exact time, depending on the adhesion as little as possible to prevent distortion. If either of the pieces has to be held by a part that

cannot be balanced between the fingers, the turning will have to be from the wrist.

Now bring the flame to bear on one spot of the joint until the wrinkles smooth out and the tube begins to collapse. Remove from the flame and blow out slightly larger than normal. Allow the part to cool slightly and repeat the process in another spot, going all around the joint without at any time allowing the entire joint to get hot enough to bend easily.

An expert glass-blower will be able to hold the parts steadily enough to heat all around, blow out and draw down to normal in one operation. Doing it peacemeal permits the making of a durable joint without much skill. When the wrinkles have been smoothed out all around, the joint will be slightly larger than normal. Heat all around again just enough to soften slightly and draw down to normal.

T-Tube.—Cut two pieces from the same piece of tubing. Heat to round the edges of both ends of the longer and of one end of the shorter piece. Allow them to cool, stopper the rounded end of the shorter tube and one end of the longer. Attach the rubber tube to the other end and blow a side hole of about the diameter of the tube. Heat the tube enough to soften it for an inch on both sides of the tube, and also heat the raw end of the shorter tube. The right temperature is shown by the appearance of sodium color in the flame. This will prevent cooling cracks. This annealing is not necessary for small tubes of new glass, but for large tubes it is a necessary precaution.

Heat the edges of the hole and the annealed end of the shorter tube and bring them together just enough to make an air-tight joint. Now bring the flame into the plane of the two tubes, bisecting the angle, until the wrinkles in the angle are smoothed out, blow out to slightly more than normal size, cool slightly and then smooth the other angle. Then smooth the sides, and, if necessary go all around again, heating and blowing, until the shape is right, but keeping one part cool enough to be stiff to prevent distortion of the tubes.

A Y-tube is made by bending one tube and blowing the hole at the angle before making the joint.

Repairing Broken Ends of Apparatus.—With a pair of sharp-edged pliers break off small pieces until the end is square. This may be done without cracking if the pliers are held firmly on a small part of the edge, without squeezing it, and then twisted outward. The thinner the glass and the larger the diameter, the smaller the bites must be, and the greater the danger of forming cracks. The pressure should not be on two points far apart on the outer edge, for fear of splitting the glass downward. If a downward crack should form, it may be led around the piece, cutting it off square. This is done by heating an iron rod red hot and pressing it on the glass near the end of the crack. The crack will advance toward the rod, and may be led in any direction. Smooth off the rough edge by rubbing it on carborundum cloth. If the piece is old, rinse it in HF. Heat it gradually by moving it through a white flame until it is covered with soot. Slowly turn on the blast, soften the edge, and make a flare or lip with the molding tool.

Ground Joints.—If a ground stopper or cap is lost or one part of a tube joint broken, it is not hard to replace it. Choose a piece a trifle smaller than the widest part of the ground surface if the new piece is to go inside, or a tube that will admit the inside piece as far as the ground part if the new piece is to go outside. This is to prevent the formation of a shoulder at one end of the joint that will confine the grinding to a narrow ring. Then draw down the end or give it a flare with the tool, to make it fit as nearly as possible, being particular to keep it round. It is better to try several times than to grind one that does not fit well.

The grinding is done by wetting the surfaces and applying powdered emery, 60-mesh or finer. The parts are ground by turning, with slight pressure, either in the same direction all the time, or else forward and back two or three times and then advancing in one direction. This keeps the ground surface round. The surfaces should be kept wet and new emery applied frequently, until a sufficient band has been ground all around the new piece. Now try whether there is a close fit without rocking. If it rocks, it is because there has been too much grinding on the sides of the band and not enough in the middle. To form a

true conical surface, use very fine emery, either so prepared, or that which has been made fine during the grinding. Every two or three turns, withdraw the piece and redistribute the emery in the joint, so that the largest pieces will grind the most convex part and the edges will not touch. The pressure should be very light at the end so that the convex part may get all the rubbing. Hard pressure, when not exactly straight, will make more grinding on the edges of the ground band, and increase the rocking. The joint is finished when it does not rock and when greased



Fig. 1.

shows a transparent band all around. Fig. 1 shows good and bad work in making the joint.

Boring Holes in Glass.—This is best done with a three-cornered file, mounted in an auger brace. The file should be of the hardest steel. The end should be ground off at an angle of 60° and the edges kept sharp by regrinding. It is used like a drill, being kept wet with turpentine saturated with camphor. Until the hole is cut through, the pressure may be as great as the thickness of

the glass will stand, but as soon as the end breaks through the pressure should be lighter to avoid splitting by turning the tool while wedged into the hole. After the hole is enlarged as much as necessary, or as the size of the drill will permit, it should be rounded with a rat-tail file. This is used by turning. The spiral grooves in a rat-tail file give it a powerful wedging action if turned so as to screw in, and in that way will split the glass. Turned against the grooves, the ridges chip out small pieces and ream out the hole without danger.

A hole may be made in glass with a file broken at the end, and held in the hand, but this is too laborious for very thick glass.

In drilling a cover glass, the work is done on the convex side, which makes splitting less likely.

A short piece of rubber tubing may be used to make a tight joint with a glass tube in the hole. The rubber must not be compressed too much, or it may split the glass.

APPARATUS

Filter Rack.—The rack shown is simple in construction, durable and easily carried about. It provides a convenient place for rods and cover glasses during filtration, and protects the filtrate from spattering. The funnel rests on three points. This makes it steady in any position, and the tip may be inclined so as to touch the side of any beaker, even if the latter is irregular in shape, to prevent splashing of the filtrate.

The slots make it easy to transfer a funnel from one place to another with the beaker under it without stopping the filtration.

They are also useful when a filtrate needs to be poured back for refiltration. The funnel is used as a pouring rod, and the operation is quickly performed without danger of losing any of the solution.

A plate should be cut as shown as a pattern for the holes. The holes are easily cut with a jig saw, which needs to follow the pattern accurately only at the three tangents of the funnel. The rack may be made narrow, with six-sided holes instead of slots and a ridge on each side to support rods. This form is lighter, but has not all the advantages of the slot form.

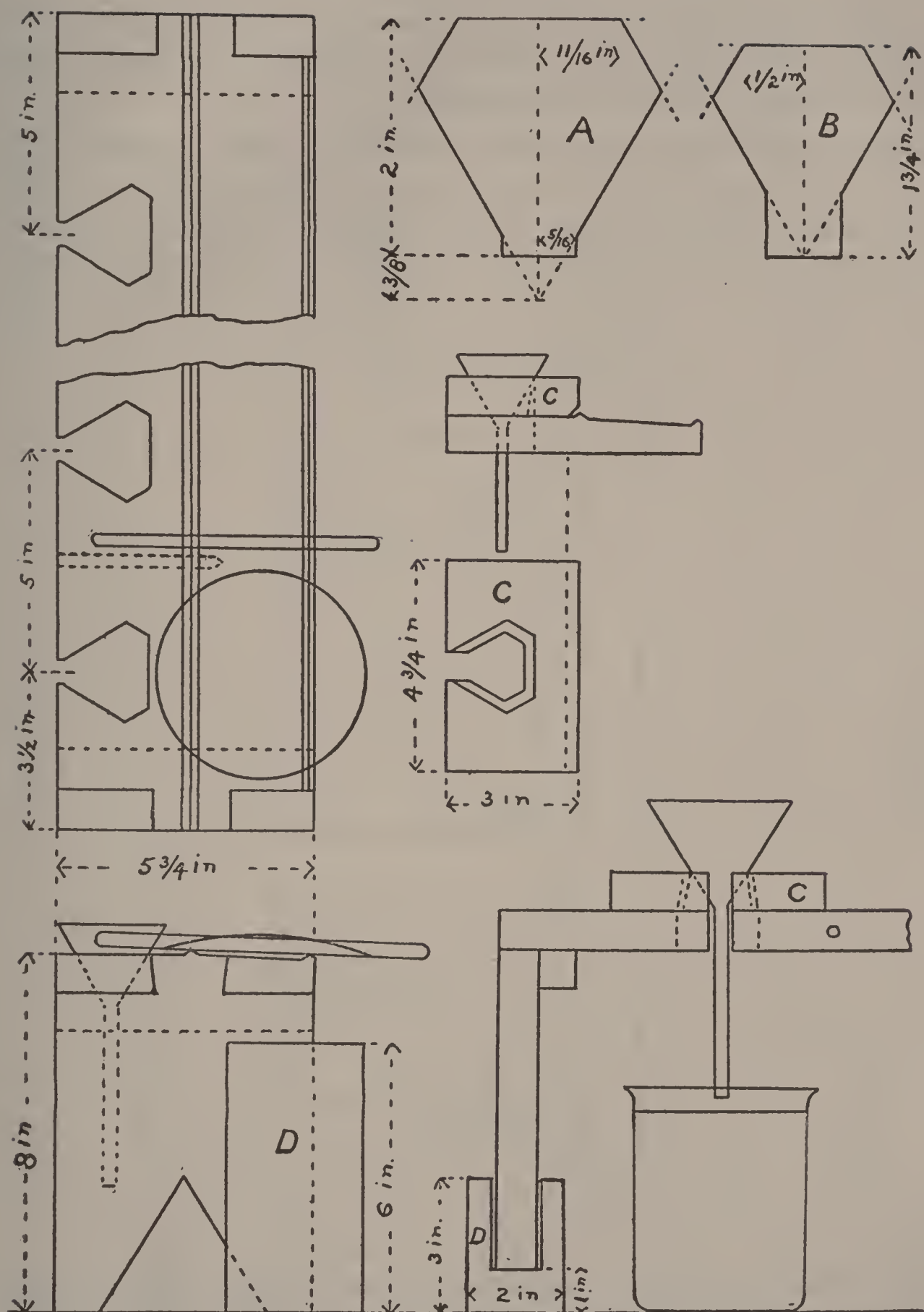


Fig. 2.

- A Development of template for notch in rack.
- B Smaller side of notch in C.
- C Funnel raiser.
- D Rack raiser.

The rack should be made of light wood that does not warp easily, such as white pine. It may be painted, though spar varnish is better. Shellac is not durable.

The sketch shows some extra pieces to be used with the rack. The end supports can be set in three positions, to raise the rack one, two, or three inches. These supports are also convenient supports for round-bottomed flasks. The horseshoe-shaped

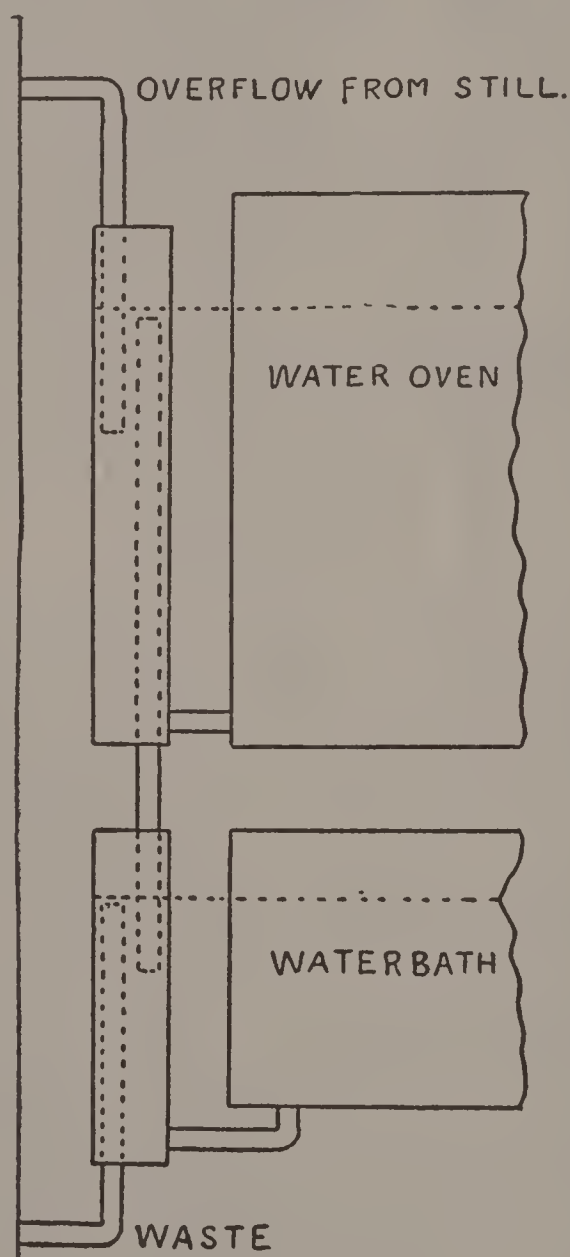


Fig. 3.

blocks are used to set funnels at different heights. As the sides of the slots in the blocks are slanting, two heights may be made according to which side is uppermost. The blocks are also used to support beakers under the rack. By the use of these extra parts filtrations of all sorts can be carried on on the same rack.

Water System.—Fig. 3 shows a convenient and economical arrangement of water flow. The still should be put in an office, or other room free from fumes and dust. The hot water from the condenser feeds the water ovens and the water baths, saving both heat and water.

Hydrogen Sulfide Generator.—The generator shown in Fig. 4 was copied from one at Cornell University. Its advantages are cheapness of construction and large capacity. It is easily kept clean by turning the hose into it, washing out the insoluble part of the iron sulfide. It would be improved by a much taller generator bottle. The back pressure of the outflow is balanced against the head of acid measured from the outlet to the point where the bubbles enter the acid bottle. The air inlet needs to turn down into a beaker to catch acid occasionally forced out by expansion of air in the acid bottle. It is necessary to have sufficient head to overcome the high surface tension of the small outlet holes and the variations caused by the emptying of the tube just above the spray when the flow ceases. The spent acid outlet must be high enough to give back pressure when the generator is clean and contains only water. Therefore the apparatus works well only when made on a large scale, with a generator bottle at least eighteen inches high.

Wash-Bottles.—When water is heated in the bottle, and when fuming solutions are used, the Bunsen valve is necessary. This may be attached to an ordinary mouth-piece inside the bottle, but in this position the rubber rapidly deteriorates, and the tube often falls off when in use. The outside valve shown in Fig. 5 lasts longer and is not so much affected by the contents of the bottle. It may be used for concentrated nitric acid or carbon disulfide.

By heating the larger end of the outer tube until it has contracted slightly, it is possible to use one piece of rubber tubing both for the valve and to seal in the mouth-piece. Rubber is best cut while wet. Sharpen a knife with a thin edge, put a small stick of wood inside the rubber tube, stretching it slightly, and cut against the wood to make a slit with smooth edges. Close the end of the tube with a rubber plug, such as is made

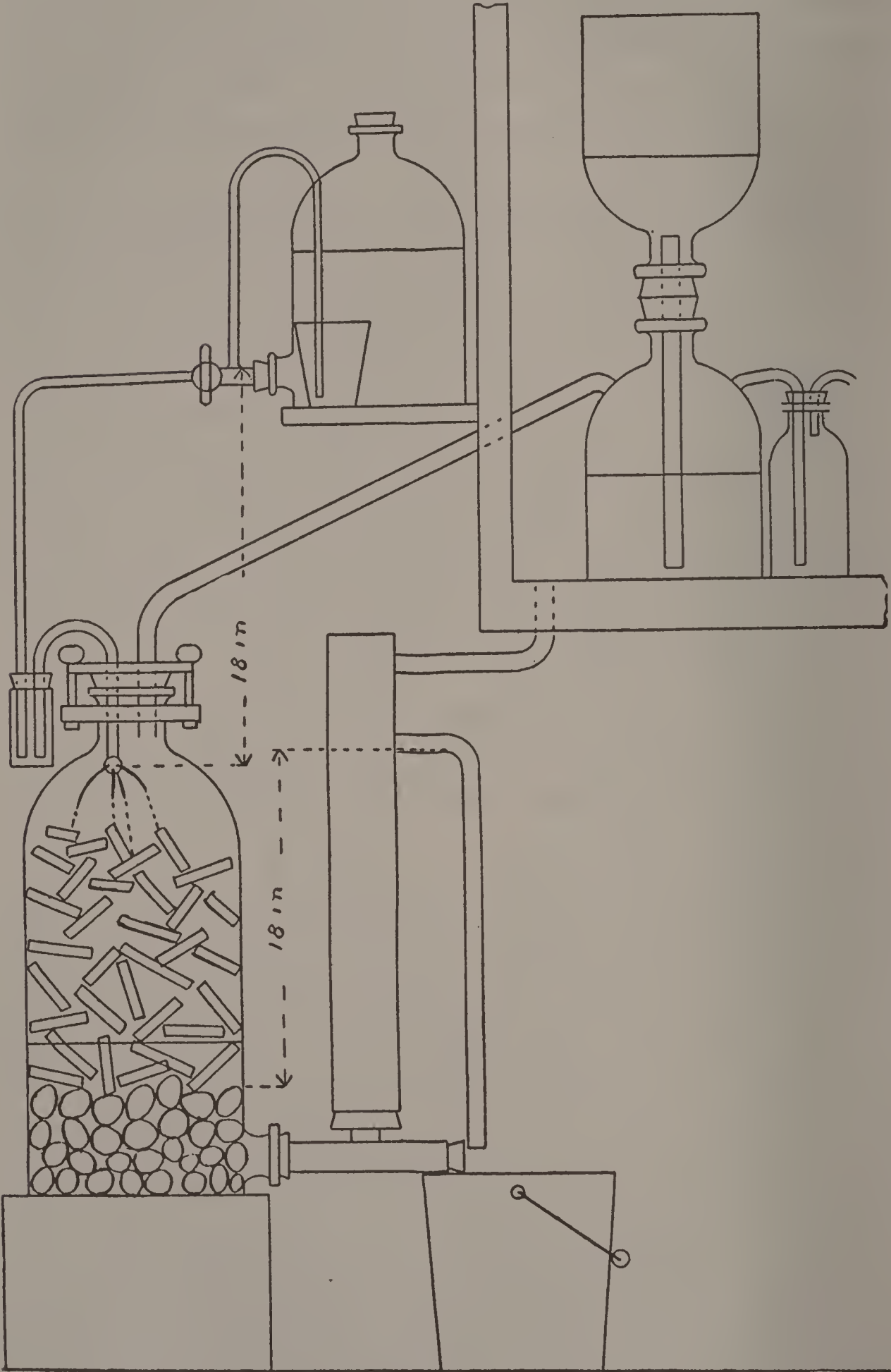


Fig. 4.

by boring a stopper. This will keep its place better than a glass plug.

A convenient insulation of the neck of the wash-bottle may be made by wrapping it in several folds of soft paper and covering the paper completely with friction tape. Fold the paper into a strip of the right width, fasten a piece of tape to the middle of the neck and then over the end of the paper strip, to assist in winding the paper on solidly. The date marked on the paper so that it can be read from the inside will make the bottle last longer.

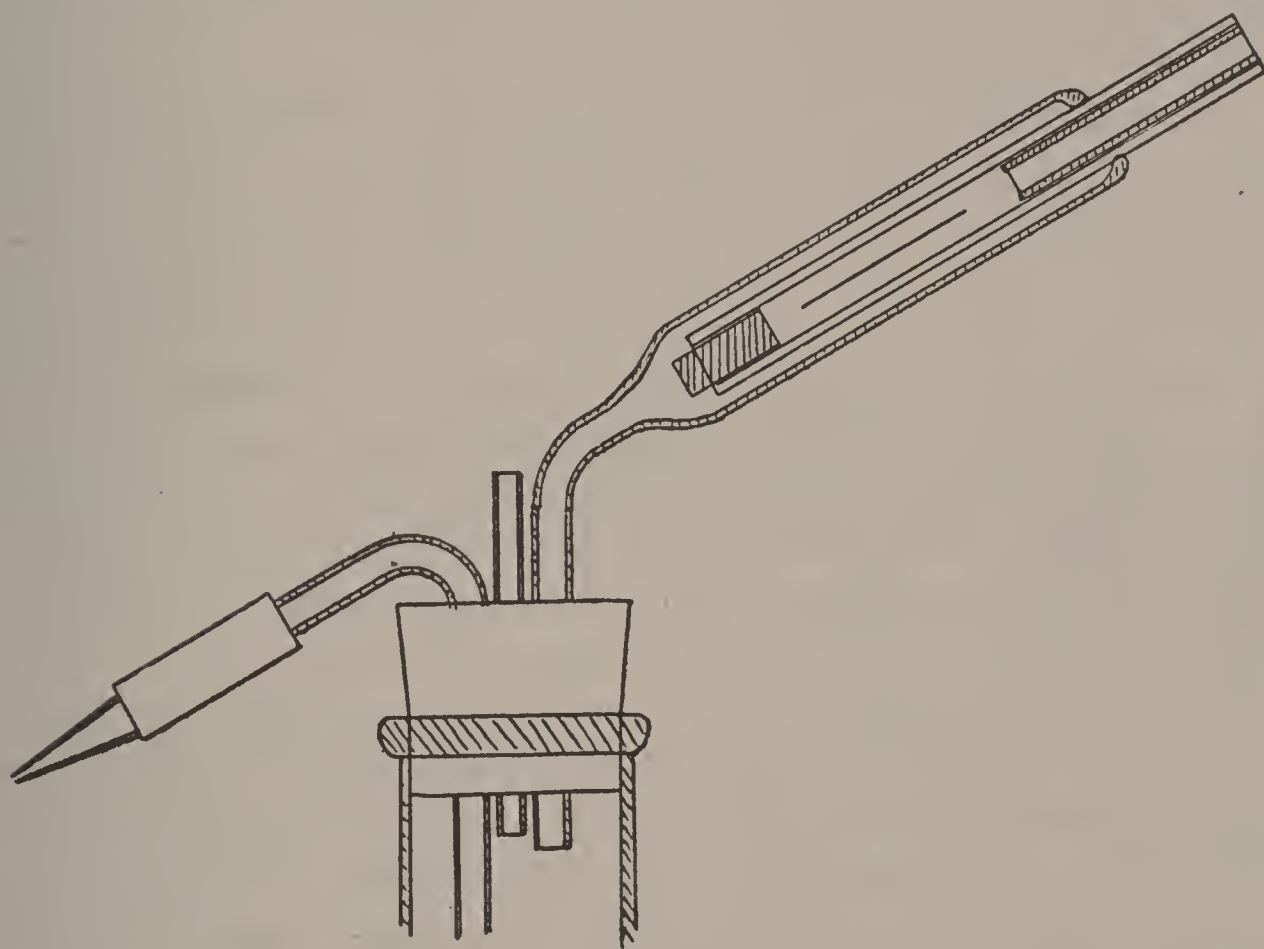


Fig. 5.

A wash-bottle will drip if the outlet tube is too large. Both the riser and the tip should be made of thick-walled tubing, of not more than four millimeters inside diameter.

It is important that the tip deliver a straight jet. To make it so, draw the tubing slowly, so that it will not become too thin, in a regular tapering shape, to the thickness desired for the end. Cool the piece, scratch it lightly with a fine sharp-edged glass knife or file, and crack it off. If the end is not square, grind it square on a piece of fine emery cloth. Wash and dry it, and

then round the end in the flame. If the aperture is too large it may be made smaller by reheating, but each time it should be heated barely to redness, cooled and tested, as it will close rapidly when soft. For ordinary work, the jet should be one millimeter in diameter.

Filters.—For filtrations which must be made rapidly, without much regard to completeness of washing, the fluted filter is the best. This should be set loosely, taking care that the tip is properly set in the neck of the funnel. If too much expanded the paper will fit tightly and cut off the channels. If pressed down too far the neck will be plugged.

The quartered or star filter is popular in colleges. By its use rapid filtration may be done with a bad funnel, but it has several disadvantages. It takes more time to fold than the ordinary filter. It is almost impossible to keep a column of liquid in the stem, so that the speed diminishes as the filter drains, and washing is slow. Owing to the inside flaps it is difficult to wash a precipitate out of it, which needs to be done in many filtering operations. Creeping precipitates are likely to get over it among its loose folds. If the filter needs to be reinforced with pulp to hold very fine precipitates much of its speed is lost. There are few cases where it has any advantage over other forms.

To use the ordinary filter with advantage a good funnel is necessary. A funnel should have a regular slope. It need not be exactly 60° , but it should not be bell-shaped or trumpet-shaped at the neck. The stem should be not less than three millimeters or more than four in internal diameter at any part. This will enable bubbles to fill it, and as they go down a suction column will be formed. A stem somewhat wider may be used if the slope is right, though it is more trouble to start the column and it may not be possible to reform it if it breaks. To keep it from breaking from below, the tip should be cut square.

Ten centimeters is an ample length for the stem. A longer stem only compacts the precipitate and gives no more speed. These dimensions apply to all sizes used for ordinary separations, up to six inches in diameter. For fluted filters a wide stem is better.

For filtering precipitates, fold the paper in half, then with the front a little less than a quarter and the back a little more, so that the angle between them is 3° or 4° for a funnel of exactly 60° . Tear off a piece one-third as deep as the radius from the front corner, using a sidewise twist so that the torn edge is beveled. Open the filter with the wide back layer single, holding the front three layers in place with the thumb and finger. Put the filter into the funnel, holding the three layers against the side, and test the angle. The paper should touch at the top and not at the bottom. Throw in water around the top, so that it runs behind the paper and starts a column, and quickly press the paper against the glass all around the top to hold the column. When wet, the paper should be free from the glass for the lower half of its height, and fit tightly at the top. If the funnel is too obtuse or too acute, raise the inner fold and change the angle of the paper to suit.

A filter made in this way takes little more time to set than one made carelessly. The speed of filtration continues until the filter is empty, making washing rapid. Precipitates do not creep over the top. Indeed, many precipitates, such as ferric oxide, are perfectly held when the funnel is filled above the paper.

If powdered gangue without any precipitate to bind it is to be filtered, as in the analysis of galena, the corner should not be torn off, as fine particles will go through the folds. The column may be secured by pouring a little pulp into the back fold and pressing it down.

Whenever a precipitate is to be washed back for decantation or for solution, the smooth inside of the ordinary filter makes it preferable to the star filter. The inner fold should be held with its edge downward in washing back.

Pulp.—Many precipitates run through ordinary filter paper at first, and when they finally filter clear run slowly. If a little loose paper pulp is put into the filter at first these precipitates, such as stannic sulfide, can be filtered clear at the start and with less clogging of the filter than when it is not used. If the corners torn from ashless papers are saved for this purpose, almost

enough pulp will be obtained for all filtrations, and only one pulp flask need be used. Most papers are broken up with difficulty by shaking with water in a flask. By adding a few glass beads or a rubber stopper, pulp can be made with less work. A whole paper is as easily broken up by shaking as when first torn into small pieces.

Some precipitates, such as ferric hydroxide, form hard grains when ignited in the ordinary way. If paper pulp is mixed with them before filtering, they form fine flaky or powdery residues on ignition. In this form they come to constant weight more readily and are more easily fused.

Reinforced Filters.—When very large filters, fifteen centimeters or more in diameter, are used, folded in the ordinary way, they are likely to break with rough handling. To guard against this, take a piece of gauze bandage an inch wide and from one to three inches long. Fold the paper in half, lay the cloth over the paper, not quite in the middle, but a little toward the wider back part of the second fold. Complete the filter as usual. The cloth will keep the filter from breaking, enable it to withstand stronger acids and alkalis than unsupported paper will, and will make filtration faster.

The Asbestos Funnel Filter.—Wet some glass wool, mold it into a ball about the size of a hazel nut, with no long fibres extending from it, and pack it into the stem of a funnel, tightly enough to keep it in place without choking the stem. Pour in a thin mixture of asbestos until the wool is well covered, and quickly follow this with water, so that a column is formed which will remain in the stem after draining. Fibres of glass running through the asbestos tend to break the column. Saturate the filter with the washing solution before using.

The Gooch Crucible.—The usefulness of this filter is greatly increased by the use of good asbestos and convenient holders for the crucibles. Gooch recommended long-fibered asbestos, and this kind is still generally used, but it is not necessarily the best. Just after the war some asbestos was imported from Italy which fulfilled every requirement. It was white and clean. When broken into short fibers and poured in a milk into the crucible it filled

every hole securely with so little material that the bottom did not need to be completely covered, each hole forming a filter by itself; and yet the filtration was rapid and ordinary precipitates did not run through. The source of this supply is not known, as the lot was bought from a jobber, and it has not appeared in the market since. In quality it must have been coarser and of more branching or rougher fibers than ordinary asbestos, though its appearance was the same under a hand glass.

American asbestos can now be bought of the sort known as "Woolly," a short-fibered by-product of the ordinary mineral, which is as rapid as this ideal material. It is not quite white and does not make so secure a filter, and more has to be put into the crucible to make a reliable mat. However, it can be used in the same way, with more care. A pulp of about 1 per cent is shaken with water and poured into the crucible with suction, until the bottom is just covered. Then the crucible is filled twice and sucked dry. Such a pad should weigh from forty to one hundred milligrams. Such precipitates as lead chromate, barium sulphate, and magnesium ammonium phosphate can be filtered perfectly with full suction on filters made in this way.

When many Gooch crucibles are used, it is a good thing to mark them.

Roughening Glazed Surfaces.—Precipitate some barium sulfate, filter it, and add to the moist pulp an equal volume of hydrofluoric acid. With a paddle apply a thick coat of this paste to a square on the crucible. Invert the crucible to prevent streaks and let it dry. This will make a matt surface suitable for marking with a lead pencil. Mark the weight of the crucible to the nearest centigram and a serial number with an A. W. Faber blue pencil No. 2251 leaving room on the square for lead pencil marks. Burn in the marks with the full heat of the blast flame, so that they become dark brown on cooling. If they are only burned red they will not be permanent.

Other glazed utensils, such as silica crucibles and the handles of casseroles, should be spotted in the same way so that they can be marked easily.

The lower parts of two empty cerusine bottles melted level by pressing on a hot plate will make a tight container for the etching paste. If the edges are pressed together they will adhere.

Gooch Crucible Holders.—There are several holders on the market, but none of them are entirely satisfactory. The holder should not collapse or come to pieces when the crucible is removed, and it should be possible to remove a crucible and set another with one hand without having to readjust the holder. The lower part of the crucible should not touch rubber, and the filtrate should pass from the crucible into glass without getting into the joint between glass and rubber. The crucible should be so held that it cannot get wedged into glass under suction, or the glass will break. It should be easy to turn the crucible during filtration, for convenience in washing.

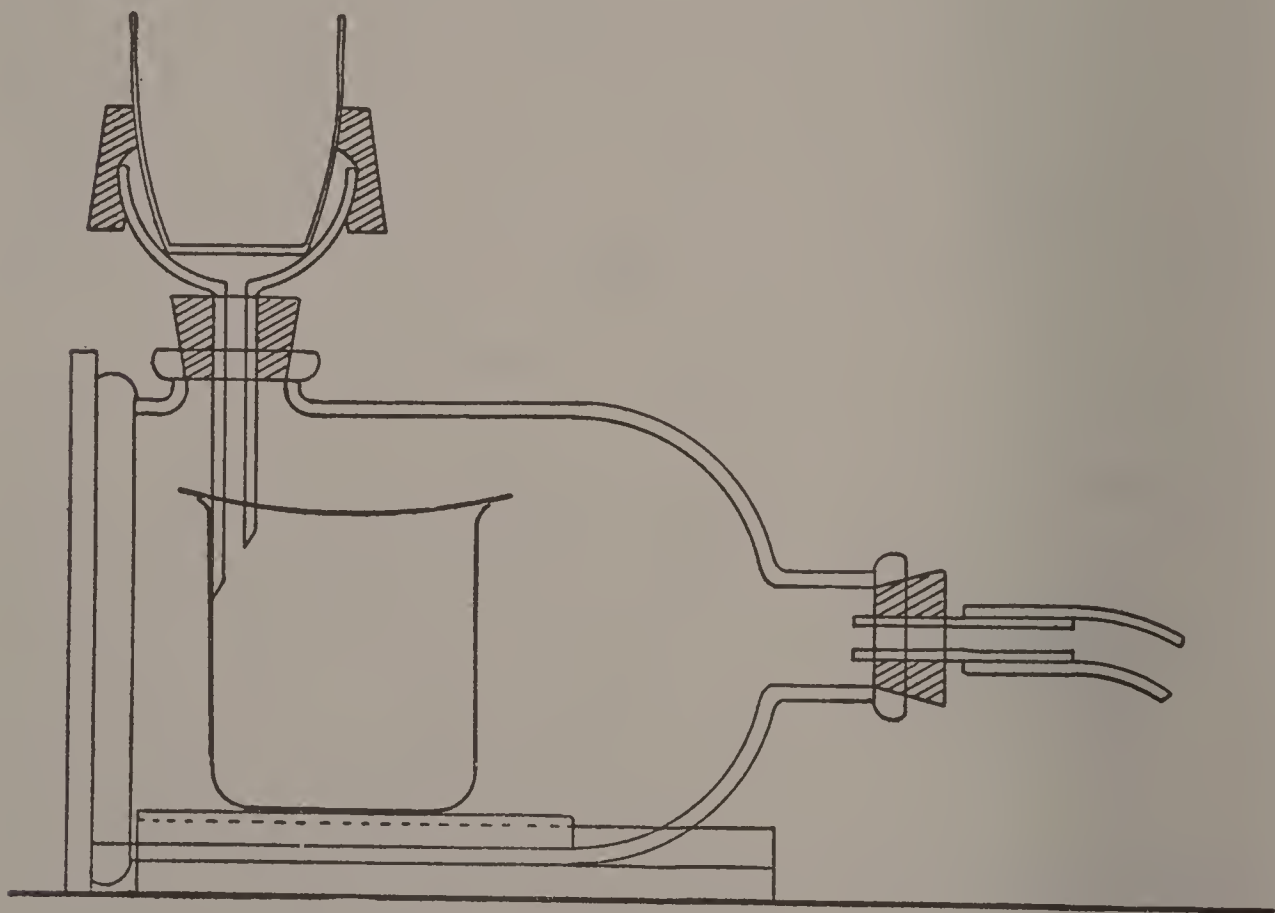


Fig. 6.

Gooch's original form met some of these requirements, but the thin rubber band would collapse and it was hard to insert the crucible. The glass tube was often broken by the suction. Other holders are free from these defects, but they do not allow the

crucible to turn. Fig. 6 shows the form of holder which the writer prefers.

The glass tube fits loosely in the rubber stopper, allowing easy turning. It is held down by suction. A bit of tubing below the stopper keeps the glass tube in place when not in use. The crucible rests on a zone of wide curvature, not quite touching the top of the glass tube, so there is no wedging. The glass rises high enough around the crucible to keep the filtrate away from the rubber band.

The band may be made from a rubber stopper. Take a piece of thin-walled brass tubing, one and one-quarter inches for the 25 cc. crucible or one and one-quarter for the 35 cc. size. With a file sharpen the end to a cutting edge. Select a stopper about three-eighths inch larger at the smaller end than the borer, and bore a hole through it. Turn the stopper inside out and cut or grind a groove about one-quarter inch from the smaller end. This groove should have the wall next the smaller end perpendicular to the axis, and should slope away toward the larger end. Turn the stopper again and fit it on the glass tube. The groove should be deep enough to allow the upper edge of the rubber to retain nearly its normal shape. The crucible will then slip in easily and be held securely.

Rubber tubing may be used, but it is hard to get the right size. If it is used, the inner edge of the band should be rounded, so that the crucible will not catch on it.

If the rubber tube is used, the holder will fit only one size of crucible; but with the bored stopper the glass tube may be wide enough to accommodate two sizes; the smaller resting on the bottom and the larger held by the rubber alone.

The glass tube for this holder may be made to order, or a "carbon filter tube" may be cut down to a height which will allow the crucible to rest on its bottom. The rubber tubing has a tendency to slip off on account of the narrow zone of contact. It may be glued in place by wetting it with strong sodium hydroxide solution and allowing it to stand for a week. If the rubber tubing available is not quite wide enough, it may be brought to the right size by stretching it over a crucible and heating it in an oven.

Ordinarily a flask is used to receive the filtrate, but sometimes it is desirable to avoid the dilution from washing out the flask. For this purpose a belljar is used, with a beaker. A perforated cover glass kept most of the spattering inside the beaker, but there is some danger of loss. Spattering may be prevented by the side-opening belljar shown in Fig. 6. If the crucible holder touches the side of the beaker the filtrate will drain quietly, though the beaker is easily displaced if the crucible is turned in washing. If the tip is enclosed in a tube of about one centimeter inside diameter, resting on the bottom of the beaker, splashing is prevented. A notched cover may be used.

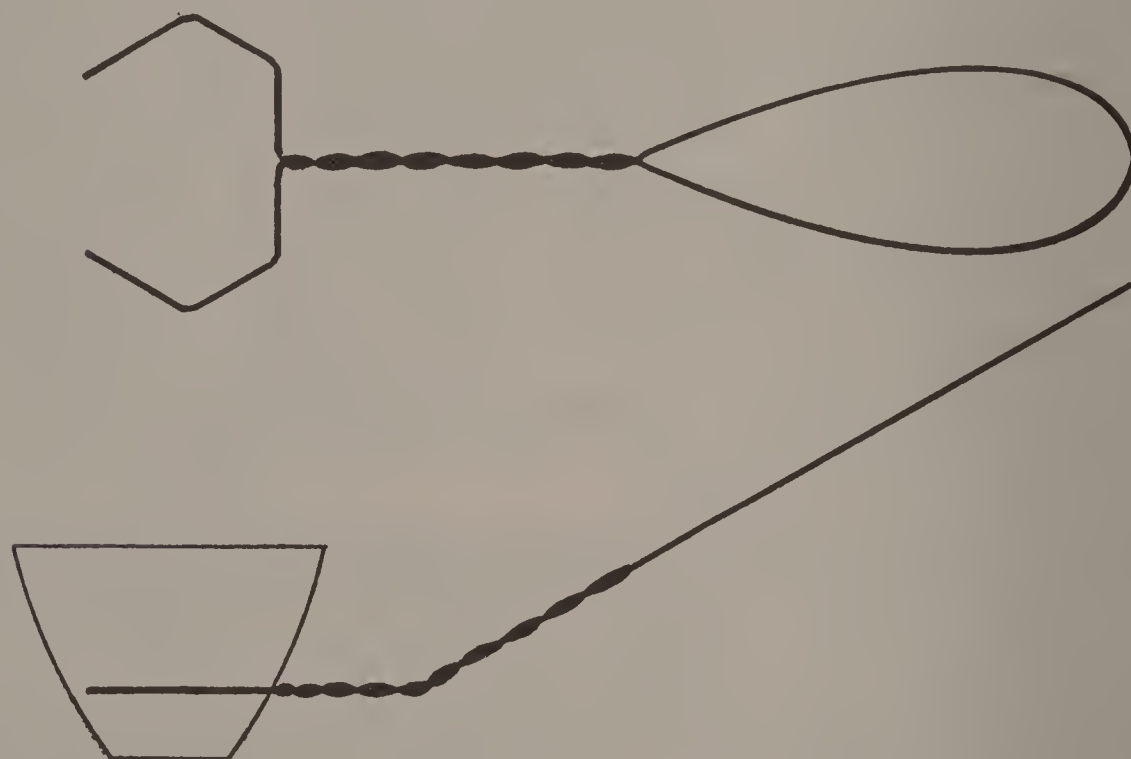


Fig. 7.

Tools for Handling Apparatus.—Fig. 7 shows a holder which is convenient for lifting crucibles containing liquid. The crucible rests on three points and cannot rock. The solid fork is more reliable than forceps, as it will not touch a cover on the crucible, will not slip, and protects the hand from the heat of the stove. There is a possibility of tilting the crucible by lifting while the fork touches the crucible only at the sides and not at the back, but with care this may be avoided. Forks of this shape with the handles turned up more may be used to transfer covered crucibles to dessicators.

Fig. 8 shows wooden tongs for flasks. They should be made of hard wood. The hinge should have a close-fitting pin, or it may be made of spring metal or leather. A glass tube may be mounted on a pair of tongs, so shaped as to direct a jet of air

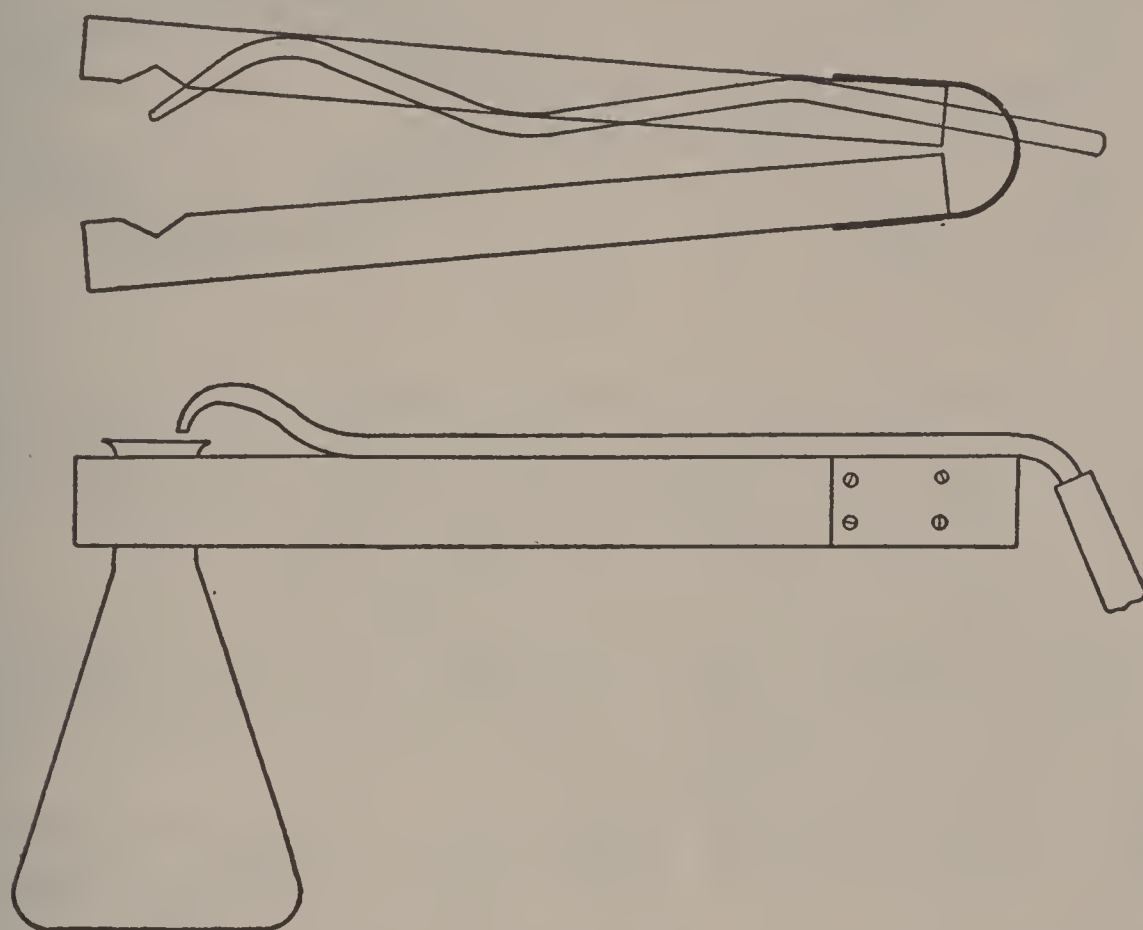


Fig. 8.

into the flask for rapid evaporation. The spring should be just strong enough to keep them open when held empty in the hand.

Fig. 9 shows beaker tongs. The grip of these tongs is not a simple V, but a compound curve, designed to give the maximum contact surface to beakers of all sizes from 100 cc. to 1,000 cc. The contact surface is extended by flattening the metal on the inside and by covering it with thick rubber tubing.

The handles are about as long as the grip, so the force required to hold a beaker is about the same as for holding it in the hand. No new habit needs to be learned in using them, and there is no danger of crushing beakers by holding them too tightly. They are real fire-proof fingers. A large beaker full of water may be held and carried by the middle, solutions may be shaken

or rotated, and beakers may be tilted for pouring as easily and securely as though held in the hand. They are particularly convenient for pouring hot acids.

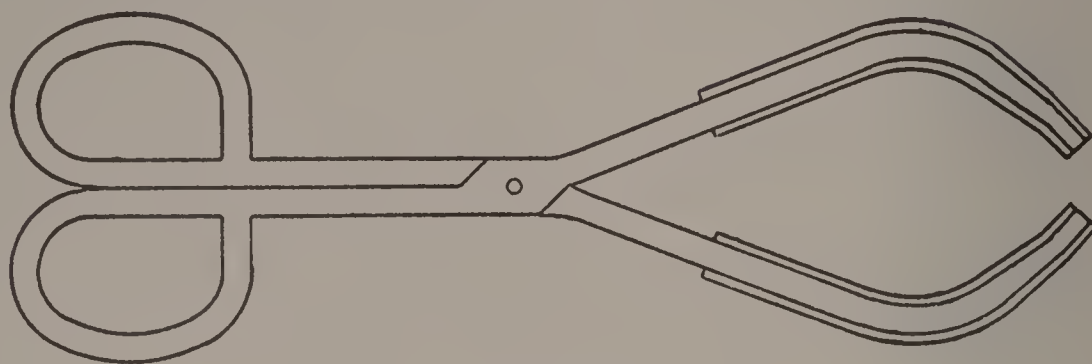


Fig. 9.

It is convenient for the chemist to carry his tongs in a pocket, so as to have them ready for emergencies and to save the trouble of hunting them when needed in different parts of the laboratory. One pair for each chemist is a complete outfit.

These tongs are sold as the "Craig Beek-tong."

Rubber Stoppers.—Only solid stoppers should be bought for laboratory use, as the holes in those bought perforated seldom fit the tubing used in apparatus.

The cork borers should be kept sharp with the special sharpener. A slight variation in bore may be made by changes in the cutting edge. If the borer is pressed hard against the cone of the sharpener and the knife pressed lightly, an outward flare is produced which makes a hole slightly larger than normal. By holding the borer lightly against the cone, inclined away from the knife, and pressing hard on the knife, the edge is crimped, producing a smaller hole.

The cores obtained by boring the stoppers are useful. A rubber plug made from one of them is better than glass in a Bunsen valve, as it never drops out.

When a tube is left in a beaker during boiling, the liquid is likely to be shot out by steam. A rubber core tapered with a knife or on an emery wheel makes a good plug.

Boring in rubber, as well as cutting with a knife, is easier if the surfaces are kept wet. Much turning and little pressure makes a smooth full-size bore.

A stopper which is used in distilling quickly takes the form into which it is compressed while hot, the holes enlarging to the size of the glass tubes. If the holes are cut in the first place approximately the size of the tubes there will be less distortion of the stopper after heating, and the fit will be as close as though the tubes had been forced into smaller holes.

Ordinary stoppers distil H_2S on the first heating with acid. Stoppers are made without sulfur, which are free from this defect. Stoppers bearing the brand E & A "Sulfree" have the added advantage of being less altered by heat than the ordinary kind, and their greater durability more than pays for their extra cost.

Policemen.—A convenient and durable policemen can be made from a rubber stopper or other piece of pure rubber. Take a No. 1 stopper and a glass rod about four-tenths by twenty centimeters. Bore a hole slightly smaller than the rod half way through the stopper from the smaller end. If the boring is done dry, friction may cause the core to break off in the borer at about the right place. If it does not, pull the core out with forceps. Wet the rod with concentrated NaOH solution and set it in the hole. In about a week the glass and rubber will be firmly cemented together.

Cut the larger end of the stopper into a wedge, taking care not to cut too close to the glass rod. Smooth the surfaces into a chisel edge on an emery wheel or cloth.

The best motion in cleaning a beaker with this policeman is up and down so that water is brought up on the sides at each stroke.

Marking on Glass and Porcelain.—A. W. Faber blue pencil No. 2,251 makes a good mark on glass, particularly if the surface is warm. It is particularly good for porcelain crucibles, as it does not run when heated, but leaves a red residue of ferric oxide. This may be made permanent by heating strongly in the blast flame.

Blaisdell red pencil No. 169 makes a good mark on glass which does not run when heated, but it burns off.

Both marks are easily removed with Gresolvent.

A cheap lead-pencil containing much clay is useful for iron and the rough bottoms of porcelain crucibles. A legible mark remains after ignition.

A recent Blaisdell product, brown laboratory pencil, No. 266 makes a permanent mark when burned. It runs when heated. Probably this defect will soon be remedied by the use of a suitable coagulant.

Pouring Bottle.—Fig. 10 shows a pouring bottle, particularly suited for ammonia. If the tip is made with care and the bore

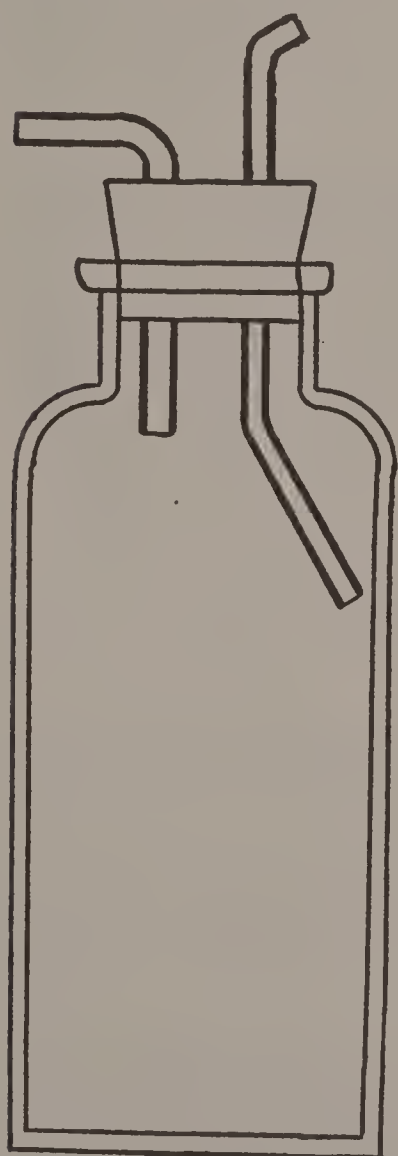


Fig. 10.

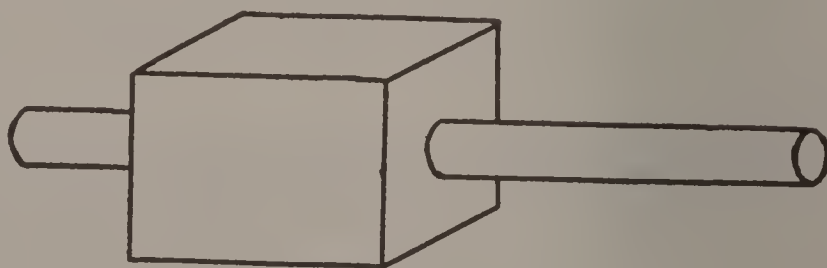


Fig. 11.

is two to two and five-tenths millimeters, it may be used like a Gay-Lussac burette, either for pouring or for dropping. In neutralizing acids with ammonia less fume is produced than when an ordinary bottle is used, and the last drops are more easily controlled.

Mouth-Piece.—When several chemists use special solution wash-bottles in common, private mouth-pieces are used. The one shown in Fig. 11 keeps the tube from touching the table when it is not in use. The tube is large enough to accommodate the largest wash-bottle tube, and the bore of the squared stopper is smaller than the tube, so that the bore of the tube is tapered to fit smaller wash-bottle tubes.

Flask Cover.—Fig. 12 shows a device for evaporating solutions from flasks. By keeping the entire flask warm, condensation on the sides is prevented, and evaporation proceeds at a

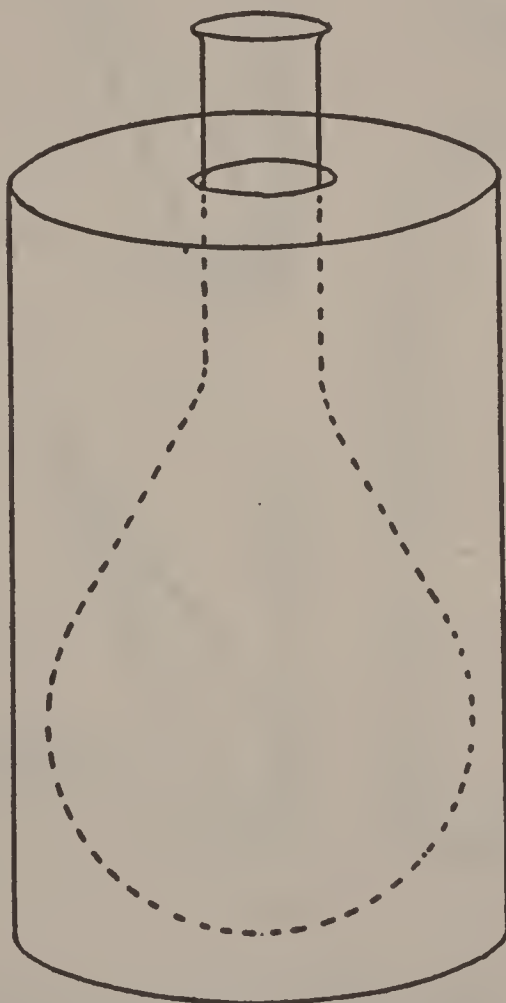


Fig. 12.

low temperature. By its use heavy liquids may be evaporated without bumping. The cover may be made from a tin can, but it is worth while to have it made higher and narrower, so that the neck can be covered and the diameter suited to the flasks used.

Dipping Pipette.—Fig. 13 shows an arrangement for measuring out reagents. The cover is made of a watch-glass or the lining

of a Mason jar lid. The pipette is kept in place by a piece of rubber tubing if the reagent does not attack it. Otherwise the tube of the pipette may be blown into a small bulb just below the cover, and a glass ferrule kept in place above it by a rubber tube or sealing wax some distance above the cover.

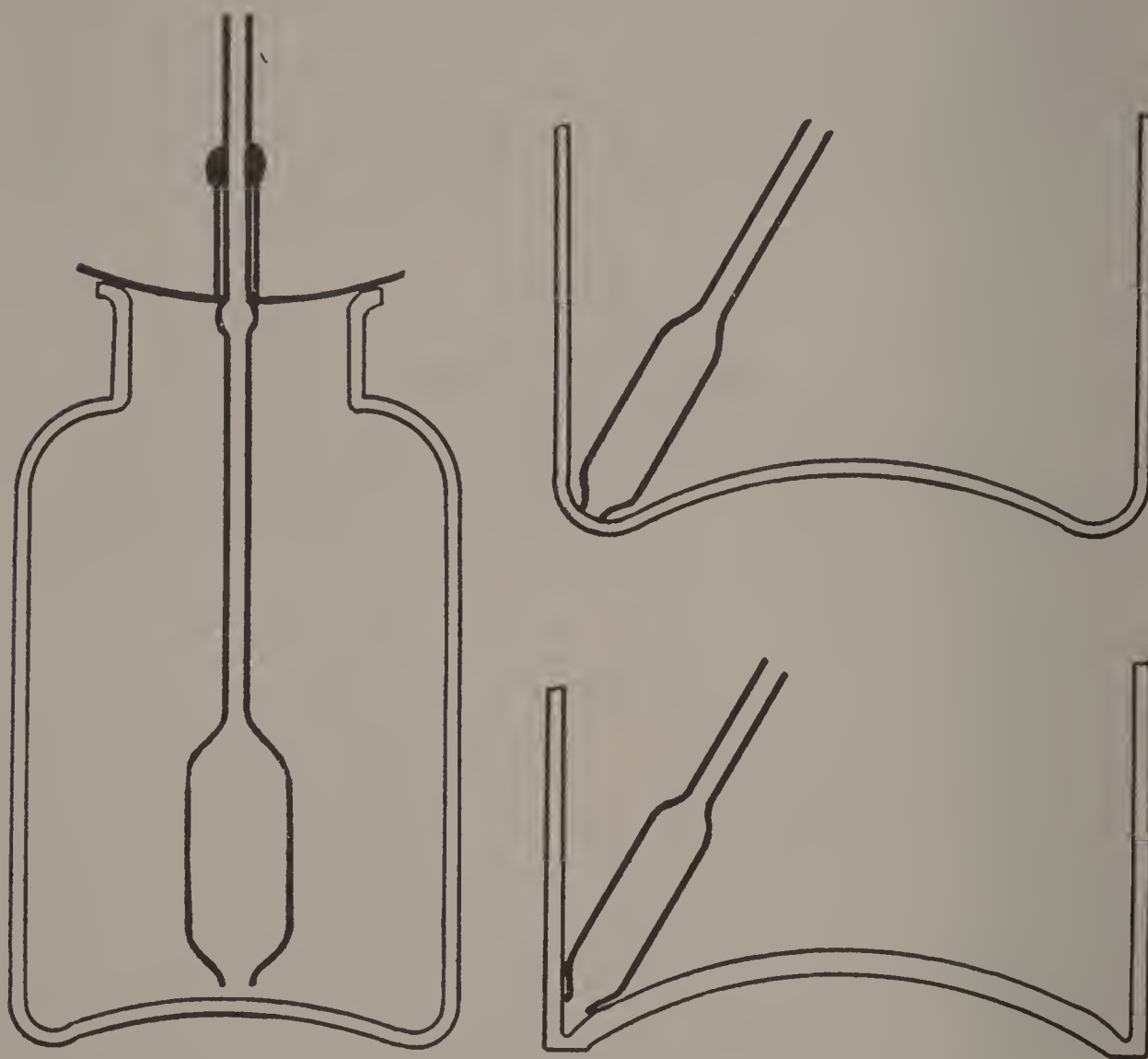


Fig. 13.

If the pipette is used without the cover, resting on the bottom of a bottle, it is important to pick a bottle like *A* and not like *B*, as the latter will catch the end of the pipette and break it.

The only important dimension of the pipette is the aperture, which should be as large as the surface tension of the liquid will permit, for speed in delivery. For H_2SO_4 the aperture should be five millimeters for any size pipette. For HNO_3 and water solutions it may be as large as six millimeters.

The Chemical Balance.—The greatest variations in the adjustment of a balance come from dirt on the beams and hangers. Aluminium particularly becomes corroded, and the oxidized parts are hygroscopic, holding different amounts of water at different temperatures. Whenever the temperature of the room changes, if the beam is dirty, the balance has to be readjusted.

Bronze beams are less subject to this variation, but it is worth while to keep the beam and hangers smooth and bright.

Some balances are equipped with two rider arms, so that one rider can be used for weighing and the other to adjust, instead of the nut at the end of the beam. Adjusting by the rider requires fewer motions, as by observing the difference in the swing the rider can be moved in most cases to the proper place at the first trial.

An adjusting rider can be used on an ordinary one-arm balance by reversing the left side hook, so that when one hook is in use the other extends backward, and only one can be lifted at a time. The extra time taken by setting the weighing rider on the beam while moving the adjusting rider, and lifting it afterward is more than made up by avoiding the air currents set up by putting the hand into the balance.

Speed in weighing is gained by setting the pan rest a little out of level, so that when it is released the needle swings a definite distance more than the difference in weight would cause. When the balance is in good condition and in adjustment, the needle will start from rest when the pan rest is lowered, and will swing exactly as far on the other side. It is therefore possible to read the needle on the half swing, instead of allowing it to return. By setting the pan rest so that the needle rests at an even division, one or two by preference, and knowing how far a milligram will carry it, the rider may be set by reading the needle to the half swing with sufficient accuracy to allow a balance in two trials after the difference has been reduced to a milligram or so.

In order to read the half swing, it is necessary to have the pan rests in good condition, so that there will be no "kick" when

they are lowered. The pads should be clean and composed of the same material, so that both may have the same elasticity and neither will stick to the pan.

Some saving in adjustment time can be gained by having a watch-glass on the pan all the time. A flat plate, either of metal or glass, instead of another watch-glass, should be used as a counterpoise on the weight side, so that the weights can be arranged in order without their sliding into a heap. A camera dry plate is about the right thickness so that a piece cut from it heavy enough to balance a watch-glass will cover the pan. A rectangular plate is better than a round one, as the weights can be arranged better on it. It is not necessary to get an exact counterpoise between the two pieces. By making the flat plate slightly lighter the difference can be made up by a piece of lead foil laid under the plate.

It is convenient to keep the fractional weights on a card glued to the floor of the balance pan. If the card is made of thick pasteboard a shallow wooden box with one side removed may be slid over the weights to protect them. The card should be marked in rectangles with a place for each weight. If the weights are then placed on the balance pan in the same relative places as on the card, they may be read more easily and accurately than if placed at random on the pan.

Adjusting Weights.—The ordinary analytical weights consist of brass for one gram and over, platinum or a gold alloy for fractional weights of five-hundredths gram and over, and aluminium for those under five-hundredths.

The brass weights are kept to standard by changing the loose material in the cavity opened by unscrewing the handle. They should be rubbed with a dry cloth until smooth before adjusting, allowing any oxide that may have formed on exposed spots to form a protective coating, rather than trying to clean the bare metal.

Platinum weights can be made up to standard when light by the addition of gold. The weight should first be cleaned in alcohol and ether, using a match-stick cut to a chisel edge to

loosen dirt. It should then be heated to redness, held with platinum-tipped forceps.

A pair of brass forceps may be tipped with pieces of platinum foil at small expense. The brass tips should be filed to parallel sides, so that rectangular pieces of foil can be tightly wrapped around them. The foil should extend about five millimeters beyond the brass. By closing the forceps tightly and pressing the two hollow extensions together with pliers, satisfactory tips can be made. The seam should be at the outside of the forceps, and may be soldered with a very small piece of solder, taking care not to allow the solder to spread to the front.

After the weight has been cleaned it should be compared with the standard and enough gold to make up the difference placed on it, preferably in the hollow of a figure, and held in the platinum forceps over a small blast flame until the gold melts and fuses into the platinum. The easiest way of getting an accurate check is to make the weight slightly heavy and then rub off the excess on a sheet of very fine emery paper, such as is used for polishing metal.

Gold and German silver weights can be spotted in the same way with tin. Silver may be used to spot gold weights if care is used to control the heat.

Aluminium weights are best cared for by rubbing enough dirt off with a stick to bring them to standard, and when too much worn, discarded.

Calibration and Use of Burettes.—In the use of burettes it is often directed to run out the solution rapidly and then wait a specified time for the sides to drain to a constant level before reading. The objections to this are, that the level of the solution in the burette rises more slowly as the drainage approaches zero and the operator is tempted to read too soon; that the proper drainage time varies with the height of column to be drained; that the solution evaporates more or less during the drainage and the reading is not exact; and that waiting for the burette to settle is an exasperating delay and consumes more time than regulating the flow.

By properly regulating the flow, the burette will drain itself as it empties, and can be read at once, the level remaining constant from the moment the flow ceases. The maximum rate which gives perfect drainage is within the limits which can be used for calibration, and a slight increase over this can be used in titrations without appreciable error, so that the burette can always be read as soon as the stop-cock is turned.

A burette should be so made that twenty drops make 1 cc. For calibration the rate of flow should be such that the water breaks into drops at the tip. For titrations the speed may be increased so that a continuous stream is half an inch long before breaking into drops. This will make a slight difference in the delivery of the burette, but not in the ratio of its parts, and if the solutions are standardized at the same rate of flow that is used for determinations, there will be no error. This rate is fast enough for most titrations, as the standard solution ought to be well mixed as it runs in, and if it runs too fast there may be an error. This is particularly true of iodine titrations.

A convenient way to calibrate a burette is to have a beaker of water of room temperature, with an accurate thermometer in it, and a long-necked flask just large enough to receive the water from the burette. The burette should be so supported that it can be read without moving it.

Weigh the flask, run in 10 cc., weigh, and so to the bottom. Refill the burette and weigh the full delivery at once. The two results should agree within five-hundredths gram.

Pipettes are calibrated in the same way, by weighing the delivered water in a flask. As solutions of varying viscosity and density are used in pipettes, experiments should be made to determine the delivery of different kinds of solutions in common use. The delivery of a pipette depends somewhat on the method of touching off the drop at the end of the delivery. The Bureau of Standards method of touching off the drop as soon as the flow ceases, on the surface of the liquid or, better, on the wet side of the container, is the quickest and most practical.

Burettes should be tested when bought, and those not sufficiently accurate sent back. Flasks and pipettes can be made more

accurate than they ordinarily are when bought ready made by buying them unmarked, calibrating them and sending them back to have the marks etched in.

The temporary mark is best made with black shellac. A glass rod drawn to a thread and wet with the shellac makes a good marker. In all such work a perfectly level table should be used, and a sight taken from the horizon or from a level mark on a window. Pipettes should be held in the hand against a frame which will hold them vertical.

The accompanying tables of corrections are taken from Circular 19 of the U. S. Bureau of Standards, entitled "Standard Density and Volume Tables."

Tables of corrections for determining the true capacities of glass vessels from the weight of water in air, using brass weights. They give the capacities in cubic centimeters at 20° C., barometric pressure seventy-six centimeters, relative humidity 50 per cent, coefficient of expansion of glass 0.000025 per degree C.

INDICATED CAPACITY 250 ML.

Temp. in Deg. C.	Tenths of degrees									
	0	1	2	3	4	5	6	7	8	9
15	0.518	0.521	0.524	0.527	0.530	0.534	0.537	0.540	0.543	0.546
16	.550	.554	.557	.560	.563	.567	.570	.574	.578	.581
17	.584	.588	.592	.596	.600	.603	.606	.610	.614	.618
18	.622	.626	.630	.634	.638	.642	.646	.650	.654	.658
19	.662	.666	.670	.674	.679	.683	.687	.692	.696	.700
20	.705	.709	.714	.718	.722	.727	.732	.736	.741	.746
21	.750	.754	.760	.764	.769	.774	.778	.784	.788	.793
22	.798	.803	.808	.813	.818	.824	.828	.834	.839	.844
23	.849	.854	.860	.865	.870	.875	.881	.886	.892	.897
24	.902	.908	.913	.919	.924	.930	.936	.941	.947	.952
25	.958	.964	.969	.975	.981	.986	.992	.998	1.004	1.010
26	1.016	1.022	1.028	1.034	1.040	1.046	1.052	1.058	1.064	1.070
27	1.076	1.082	1.089	1.095	1.101	1.108	1.114	1.120	1.126	1.132
28	1.139	1.146	1.152	1.158	1.165	1.172	1.178	1.184	1.191	1.198
29	1.204	1.211	1.218							

INDICATED CAPACITY 200 ML.

Temp. of Deg. C.	Tenths of degrees									
	0	1	2	3	4	5	6	7	8	9
15	0.414	0.417	0.419	0.422	0.424	0.427	0.430	0.432	0.435	0.437
16	.440	.443	.445	.448	.451	.454	.456	.459	.462	.465
17	.468	.470	.473	.477	.479	.482	.485	.488	.491	.494
18	.497	.501	.504	.507	.510	.513	.516	.519	.523	.526
19	.529	.533	.536	.540	.543	.546	.550	.553	.557	.560
20	.564	.567	.571	.574	.578	.582	.585	.589	.593	.596
21	.600	.604	.608	.612	.615	.619	.623	.627	.631	.635
22	.639	.643	.647	.650	.655	.659	.663	.667	.671	.675
23	.679	.683	.688	.692	.696	.700	.705	.709	.713	.717
24	.722	.726	.731	.735	.739	.744	.748	.753	.757	.762
25	.766	.771	.775	.780	.785	.789	.794	.799	.803	.808
26	.813	.818	.822	.827	.832	.837	.842	.846	.851	.856
27	.861	.866	.871	.876	.881	.886	.891	.896	.901	.906
28	.911	.917	.922	.927	.932	.937	.942	.947	.953	.958
29	.963	.969	.974							

INDICATED CAPACITY 150 ML.

Temp. in Deg. C.	Tenths of degrees									
	0	1	2	3	4	5	6	7	8	9
15	0.311	0.313	0.314	0.316	0.318	0.320	0.322	0.324	0.326	0.328
16	.330	.332	.334	.336	.338	.340	.342	.344	.346	.349
17	.351	.353	.355	.357	.359	.362	.364	.366	.368	.371
18	.373	.375	.378	.380	.383	.385	.387	.390	.392	.395
19	.397	.400	.402	.405	.408	.410	.412	.415	.418	.420
20	.423	.425	.428	.431	.433	.436	.439	.442	.445	.448
21	.450	.453	.456	.459	.461	.464	.467	.470	.473	.476
22	.479	.483	.485	.488	.491	.494	.497	.500	.503	.506
23	.509	.512	.516	.519	.522	.525	.529	.532	.535	.538
24	.541	.545	.548	.551	.554	.558	.562	.565	.568	.571
25	.575	.578	.581	.585	.588	.592	.596	.599	.602	.606
26	.610	.613	.617	.620	.624	.628	.631	.635	.638	.642
27	.645	.649	.653	.657	.661	.664	.668	.672	.676	.680
28	.684	.688	.691	.695	.699	.703	.707	.711	.715	.719
29	.722	.726	.730							

INDICATED CAPACITY 100 ML.

Temp. in Deg. C.	Tenths of degrees									
	0	1	2	3	4	5	6	7	8	9
15	0.207	0.208	0.210	0.211	0.212	0.213	0.215	0.216	0.217	0.219
16	.220	.221	.223	.224	.225	.227	.228	.230	.231	.232
17	.234	.235	.237	.238	.240	.241	.243	.244	.246	.247
18	.249	.250	.252	.253	.255	.257	.258	.260	.261	.263
19	.265	.266	.268	.270	.272	.273	.275	.277	.278	.280
20	.282	.284	.285	.287	.289	.291	.293	.294	.296	.298
21	.300	.302	.304	.306	.308	.310	.312	.314	.315	.317
22	.319	.321	.323	.325	.327	.329	.331	.333	.336	.338
23	.340	.342	.344	.346	.348	.350	.352	.354	.357	.359
24	.361	.363	.365	.368	.370	.372	.374	.376	.379	.381
25	.383	.386	.388	.390	.392	.395	.397	.399	.402	.404
26	.406	.409	.411	.414	.416	.418	.421	.423	.426	.428
27	.431	.433	.436	.438	.440	.443	.446	.448	.451	.453
28	.456	.458	.461	.463	.466	.469	.471	.474	.476	.479
29	.482	.484	.487							

INDICATED CAPACITY 50 ML.

Temp. in Deg. C.	Tenths of degrees									
	0	1	2	3	4	5	6	7	8	9
15	0.104	0.104	0.105	0.106	0.106	0.107	0.107	0.108	0.109	0.109
16	.110	.111	.111	.112	.113	.113	.114	.115	.116	.116
17	.117	.118	.118	.119	.120	.121	.121	.122	.123	.124
18	.124	.125	.126	.127	.128	.128	.129	.130	.131	.132
19	.132	.133	.134	.135	.136	.137	.137	.138	.139	.140
20	.141	.142	.143	.144	.144	.145	.146	.147	.148	.149
21	.150	.151	.152	.153	.154	.155	.156	.157	.158	.159
22	.160	.161	.162	.163	.164	.165	.166	.167	.168	.169
23	.170	.171	.172	.173	.174	.175	.176	.177	.178	.179
24	.180	.182	.183	.184	.185	.186	.187	.188	.189	.190
25	.192	.193	.194	.195	.196	.197	.199	.200	.201	.202
26	.203	.204	.205	.207	.208	.209	.210	.212	.213	.214
27	.215	.216	.218	.219	.220	.222	.223	.224	.225	.226
28	.228	.229	.230	.232	.233	.234	.236	.237	.238	.240
29	.241	.242	.244							

INDICATED CAPACITY 40 ML.

Temp. in Deg. C.	Tenths of degrees									
	0	1	2	3	4	5	6	7	8	9
15	0.083	0.083	0.084	0.084	0.085	0.085	0.086	0.086	0.087	0.087
16	.088	.089	.089	.090	.090	.091	.091	.092	.092	.093
17	.094	.094	.095	.095	.096	.096	.097	.098	.098	.099
18	.099	.100	.101	.101	.102	.102	.103	.104	.105	.105
19	.106	.107	.107	.108	.109	.109	.110	.111	.111	.112
20	.113	.113	.114	.115	.116	.116	.117	.118	.119	.119
21	.120	.121	.122	.122	.123	.124	.125	.125	.126	.127
22	.128	.129	.129	.130	.131	.132	.133	.133	.134	.135
23	.136	.137	.138	.138	.139	.140	.141	.142	.143	.143
24	.144	.145	.146	.147	.148	.149	.150	.151	.151	.152
25	.153	.154	.155	.156	.157	.158	.159	.160	.161	.162
26	.163	.164	.164	.165	.166	.167	.168	.169	.170	.171
27	.172	.173	.174	.175	.176	.177	.178	.179	.180	.181
28	.182	.183	.184	.185	.186	.187	.188	.189	.191	.192
29	.193	.194	.195							

INDICATED CAPACITY 30 ML.

Temp. in Deg. C.	Tenths of degrees									
	0	1	2	3	4	5	6	7	8	9
15	0.062	0.063	0.063	0.063	0.064	0.064	0.064	0.065	0.065	0.066
16	.066	.066	.067	.067	.068	.068	.068	.069	.069	.070
17	.070	.071	.071	.071	.072	.072	.073	.073	.074	.074
18	.075	.075	.076	.076	.077	.077	.077	.078	.078	.079
19	.079	.080	.080	.081	.081	.082	.082	.083	.084	.084
20	.085	.085	.086	.086	.087	.087	.088	.088	.089	.089
21	.090	.091	.091	.092	.092	.093	.093	.094	.094	.095
22	.096	.096	.097	.098	.098	.099	.099	.100	.101	.101
23	.102	.103	.103	.104	.104	.105	.106	.106	.107	.108
24	.108	.109	.110	.110	.111	.112	.112	.113	.114	.114
25	.115	.116	.116	.117	.118	.118	.119	.120	.121	.121
26	.122	.123	.123	.124	.125	.126	.126	.127	.128	.128
27	.129	.130	.131	.131	.132	.133	.134	.134	.135	.136
28	.137	.137	.138	.139	.140	.141	.141	.142	.143	.144
29	.145	.145	.146							

Example of Use of Table.—Determination of the capacity of a glass measuring flask marked “to contain 250 milliliters at 20° C.”

Apparent weight of water at the observed temperature 22.3° C.	249.198 g.
Correction from table	0.813
	<hr/>
Actual capacity in ml. or cc. at 20°	250.011

CHAPTER II

TABULATION METHOD FOR DIRECT RATIOS

This method is useful for chemical calculations, in which most ratios are direct. It furnishes a convenient scheme for recording data and results, and serves as a guide to the solution of problems.

Rule 1.—In any problem, make a series of columns, heading each with the name of a kind of quantity, so that all quantities of the same kind shall be in the same column.

Rule 2.—Quantities in the same horizontal line must be known to have a constant relation to each other. All must be facts which are at the same time true in a particular case, expressed in quantities described by the column headings.

Rule 3.—If any four quantities in different parts of the chart form a rectangle, the product of two diagonally opposite corners is equal to the product of the other two corners, by proportion.

If three corners of a rectangle are filled the fourth may be found by multiplying the pair of diagonals and dividing by the third, as in proportion.

Rule 4.—Rectangles may be filled in any order, beginning with one having three known quantities, but there is often economy of attention and work in filling corners on the same line, either horizontal or vertical, with the position of the desired result.

Rule 5.—Before beginning the calculation, tabulate all data relating to the problem, allowing space for additions and subtractions due to back titrations and similar procedures in which the algebraic sum of two or more quantities is the measure of the element to be determined.

Locate on the chart the position of the desired result, and mark it with braces (). Then mark the position which must be filled in order to have three known quantities in a rectangle with the position of the result, making as few steps as possible.

Fill the rectangles by calculation, beginning with the one which has three corners filled.

Rule 6.—The calculation may be checked by filling rectangles not used in the first solution until the desired position has been reached.

Rule 7.—Any problem or part of a problem in which there are no additions may be solved by logarithms. Locate all the rectangles necessary to the solution. Take the first rectangle, set down the logarithms of the diagonals and the cologarithm of the odd corner. The sum of these gives the logarithm of the fourth corner. Take the next rectangle containing this corner, put down in the column the logarithm of its diagonal and the cologarithm of its vertical or horizontal mate. The sum is the logarithm of the fourth corner of the second rectangle. Proceed in this way until the result has been reached, solving for it alone, or for all the intermediate quantities, as desired.

In the examples, the data found by observation are under-scored. All quantities obtained from other sources, such as handbooks, are marked by "quotes." Quantities obtained by calculation in the first solution are enclosed in (braces). The second line of calculation is left unmarked. In actual use, only the braces need be used.

Example 1.—How many cubic centimeters of nitric acid, 69.8 per cent pure, specific gravity 1.42, will make a liter of normal solution?

Cc. normal solution	Grams pure HNO_3	Grams reagent HNO_3	Cc. reagent HNO_3
"1,000	63.018"	90.28	(63.58) 63.58
15.728"	(0.99116)	"1.42	1"
	69.8"	100"	

By definition, a liter of normal acid contains one hydrogen equivalent, in this case one gram molecule. Specific gravity in the metric system is numerically the same as density, the weight in grams of one cubic centimeter. The expression "69.8 per cent pure" means that 100 parts by weight of a given material contains 69.8 parts by weight of the pure substance named. Both percentage and specific gravity are ratios, and each is expressed by two quantities in different columns.

The preferred solution of this problem does not follow Rule 4, because the intermediate step showing grams HNO_3 per cc. is itself a useful figure. Incidentally the normal strength of the reagent, 15.728, is easily found.

Example 2.—In the reaction $3 \text{SnCl}_2 + 4 \text{HCl} + \text{KClO}_3 = \text{KCl} + 3 \text{SnCl}_4 + 2 \text{H}_2\text{O}$, how many grams of KClO_3 will be required for 5 grams of Sn, and how many cc. of reagent HCl, 37.23 per cent pure, specific gravity 1.19, will be neutralized?

Grams Sn	Grams HCl	Grams KClO_3	Grams reagent HCl	Cc. reagent HCl
5	(2.0434)	(1.717)	(54.89)	(4.61) 4.61
"357	145.90"	122.56"		329.3
			"1.19	1"
	"37.23		100"	81.04

Here the multiples of the molecular and atomic weights are obtained from the coefficients in the equation. As these may be expressed in any unit, it is legitimate to put them in the same column with grams actually weighed.

Example 3.—A sample of commercial sulfuric acid was assayed as follows. Having some solutions approximately 0.2 N NaOH and 0.5 N HCl, they were titrated against each other and against Na_2CO_3 . To titrate the sample, some of it was weighed into a beaker, slightly less than its equivalent of Na_2CO_3 was weighed into it, the CO_2 boiled out, and the excess titrated with

Cc. NaHO	Cc. HCl	Grams Na_2CO_3	Cc. normal	Grams sample	Grams H_2SO_4	Grams Fe_2O_3	Grams ZnO
(89.55)	36.70	1.0013	(18.892)				
24.40	10.00						
4.7402	1.9427	"0.00530025	1"		0.049043"	0.0266"	0.0407"
(1)			(0.2110) 0.2110		0.010348		
	(1)		(0.5148) 0.5148				
13.20		4.0507	+ 2.785 + 76.425 — 0.241 — 0.074 78.895		(+0.1366) (+3.7481) (—0.0118) (—0.0036) (3.8692)	0.0064	0.0030
			5.1175 "100"		(75.61)		

NaOH. After titrating a precipitate was found, the bases in which were originally combined with the acid, making it necessary to deduct their acid equivalents from the titration figure in order to show the free acid. All the data were referred to H_2SO_4 . As a check, the data were referred to normal solution.

Example 4.—A sample of copper was assayed for S by conversion to H_2S in a stream of H and titration with iodine by the reaction $\text{H}_2\text{S} + 2 \text{I} = 2 \text{HI} + \text{S}$. On a 95-gram sample 0.35 cc. of I solution was used. The iodine was standardized against As_2O_3 dissolved in HCl by the reaction $\text{AsCl}_3 + 2 \text{HCl} + 2 \text{I} = \text{AsCl}_5 + 2 \text{HI}$. Twenty-five hundredths gram of As_2O_3 required 49.25 cc. of I solution.

What is the percentage of S in the sample?

Grams of sample	Grams of S	Cc. I solution	Grams of As_2O_3
<u>95</u>	(0.000576)	(0.35)	
		<u>49.25</u>	<u>0.25</u>
	"64.14"		"197.92"
	(0.001645)	<u>I</u>	(0.005076)
<u>100</u>	(0.000606)		

The calculation may be made by logarithms as follows:

x	0.25	9.39794 - 10
x	1.00	0
÷	49.25	8.30759 - 10
x	64.14	1.80713
÷	197.92	7.70351 - 10
x	0.35	9.54407 - 10
÷	1.00	0
x	100.00	2
÷	95.00	8.02228 - 10

$$6.78252 - 10 = 0.000606 = \text{Per cent.}$$

Example 5.—Given the following data, calculate the percentage of Fe in a sample of crude ferric chloride weighing 1 gram. The I liberated by the reaction $2 \text{FeCl}_3 + 2 \text{HI} = 2 \text{HCl} +$

$2 \text{FeCl}_2 + \text{I}_2$ is reduced by the addition of 50 cc. of $\text{Na}_2\text{S}_2\text{O}_3$ solution and the excess titrated with standard I solution, and requires 7.85 cc. 45 cc. of I solution = 45.95 cc. of $\text{Na}_2\text{S}_2\text{O}_3$ solution. 45 cc. of As_2O_3 solution = 45.27 cc. of I solution. 1 cc. of As_2O_3 solution = 0.005160 gram of As_2O_3 .

Grams of sample	Grams of Fe	Cc. of I solution	Cc. of $\text{Na}_2\text{S}_2\text{O}_3$ so	Grams of As_2O_3 so	Grams of As_2O_3
			50.00		
		7.85	(8.02)		
I	()		(41.98)		
	()	45.00	45.95		
	()	45.27		45.00	
	()			1.00	0.005160
	"55.84"				49.48"
100	(23.79)				

In solving this problem the first step is to find the thiosulfate value of the iodine used in titrating back, and then by subtraction find the amount of thiosulfate reacting with iron. By keeping in mind the order of operations, problems of this sort can be tabulated completely before beginning the calculation. After completing the subtraction, the other rectangles can be stepped off to the final logarithm without solving for the intermediate numbers.

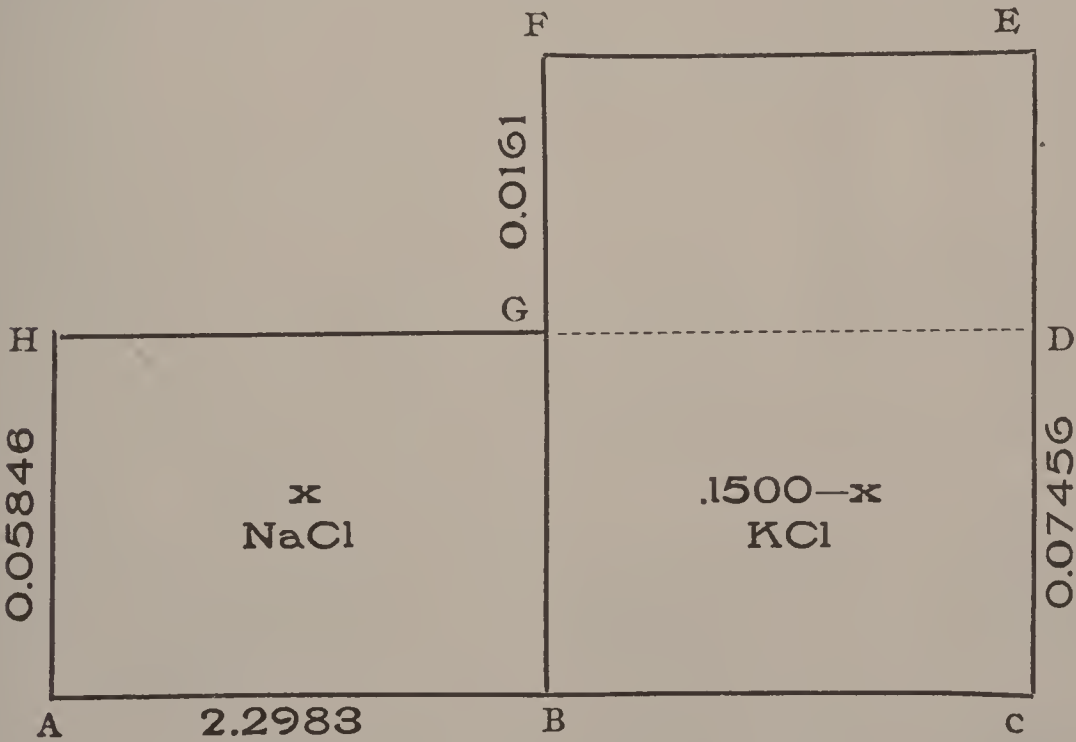
The calculation is as follows:

x 7.85	0.8949	x 0.00516	7.7126 - 10
x 45.95	1.6623	x 55.84	1.7469
÷ 45.00	8.3468 - 10	÷ 49.48	8.3056 - 10
		x 45.00	1.6532
	0.9040 = 8.017	÷ 1.00	0.0000
		x 45.00	1.6432
		÷ 45.27	8.3442 - 10
	50.00	x 41.98	1.6230
	8.02	÷ 45.95	8.3377 - 10
		x 100.00	2.0000
	41.98	÷ 1.00	0.0000
			1.3764 = 23.79

Example 6.—A mixture of pure chlorides of sodium and potassium from 0.5 gram of feldspar weighs 0.1500 gram, and after solution in water requires 22.71 cc. of 0.1012 N silver nitrate for the precipitation of the chloride ions. What are the percentages of Na₂O and K₂O in the sample?

Grams of sample	Grams of NaCl	Grams of Na ₂ O	Grams of KCl	Grams of K ₂ O	Cc. of AgNO ₃	Cc. normal
					"1	0.1012"
0.5					22.71	(2.2983)
	(x=0.07756)	(0.04113)				(y = 1.3267)
			(0.1500 — x) (= 0.07244)	(0.04576)		(2.5983 — y) (= 0.9714)
	"0.05846	"0.0310	"0.07456	"0.04710		1"
100		(8.23)		(9.15)		

This problem is solved by algebra, or it may be visualized geometrically by taking advantage of the fact that the unknown quantities are in proportion with 1 cc. normal, so that in each case one unknown is the numerical product of two other numbers. As a product may be represented by the area of a rectangle of which the factors are the sides, the solution is as follows.



Representing the value of 1 cc. normal in grams of the two chlorides as ordinates and the number of cc. as the abscissa, the area ACEFGH = 0.1500, the combined weight of the chlorides. From these figures we can obtain the area ACDH, and

by subtraction $GDEF = 0.01564$. Dividing this by 0.0161 we obtain 0.9714, the number of cc. N consumed by KCl, and by subtraction 1.3269 cc. consumed by NaCl, and so on.

This method leads to a formula for averaging the results of an assay made on two portions of a sample separately. When one of the portions is very small and of high assay, as in the case of metallica in an ore, it is convenient to reduce the assay of the metallica to a correction to be added to the assay of the fine. The correction being small the calculation is less laborious.

The proportions of fine and metallica being recorded in percentage, the abscissa becomes 100, and the two ordinates the assays of the fine and metallica, either in percentage or ounces per ton. The area of the rectangle above the dotted line, GDEF, is exchanged for one of length 100, the height of which is the correction to be added.

Multiply the difference between the two assays by the percentage of the portion having the higher assay, divide by 100, and add the quotient to the lower assay.

CHAPTER III

SOME PROPERTIES OF THE COMMONER ELEMENTS

Hydrogen.—H, heads the list in the periodic system with but slight tendencies toward either acid or alkaline properties, being midway in the electro-potential series. It forms the positive ion in all acids, and is included in the negative ion of the weakest of acids, HOH.

H is of one valence, 1.

H is ordinarily weighed as water, by absorption in H_2SO_4 or CaCl_2 .

Oxygen.—O, like H, has no decided acid or alkaline properties of its own, though in combination it is generally found in the negative ion.

Its valence is constant, 2.

It is weighed generally as H_2O .

Nitrogen.—N heads the fifth group, of generally acid tendencies, though forming part of the positive ion NH_4 .

The commoner valences of N are 3 and 5, being more stable in the latter condition. By the action of metals HNO_3 is reduced to NO, but its reduction is not the basis of titration.

It forms no weighable insoluble compounds, and in all of its forms it is volatile at temperatures below redness.

It is determined by reduction to NH_4OH in alkaline solution by the action of metals, distilled and titrated as an alkali.

Carbon.—C inclines slightly to the acid side in its commonest form, CO_2 . Electrolytically it is negligible.

With the one exception of CO, its valence is 4, and its reduction is not an analytical procedure.

It is insoluble as C, and is weighed as such when so found in the sample. In analysis it is weighed as CO_2 by absorption in alkalies, or as BaCO_3 .

Boron.—B is notable for being in most forms involatile, yet being assayed by distillation.

B has a valence of 3, and is not reduced under laboratory conditions. Its common compounds are the borates, compounds of the oxyacid B(OH)_3 , such as NaBO_2 and $\text{Na}_2\text{B}_4\text{O}_7$.

B forms no weighable precipitates. It is distilled as methyl borate $B(OCH_3)_3$, and the distillate may be weighed. This vapor gives a green flame color.

$B(OH)_3$ bleaches phenolphthalein but does not redden methyl orange. Titration methods are based on this difference from other acids, CO_2 being easily expelled.

Silicon.—Si succeeds C in Group IV of the periodic system, with decidedly acid properties.

It has a practically constant valence of 4, and its reduction to Si is a matter of great difficulty.

It is weighed as SiO_2 .

SiF_4 is gaseous. In the presence of chlorides, Si is slightly volatile at high temperatures by the formation of $SiCl_4$, so that thorough washing of SiO_2 is necessary, with careful roasting before ignition.

H_4SiO_4 , when produced in solution by adding acid to silicates, will remain completely in solution in a concentration as great as 1 per cent, but by evaporation or the use of coagulants gelatinous H_2SiO_3 is partly precipitated, which cannot be filtered, as it clogs the filter. SiO_2 must either be kept in solution or else made insoluble by drying. Perfect precipitation is a matter of the greatest difficulty, as too high a temperature causes the reformation of soluble silicates. A practical limit of drying temperature is 130° .

Sulfur.—S follows O in the series, having in common with it the ability to form electro-negative ions with other elements, as in the case of HSH. With O it forms strong acids.

Its valences are 2, 4 and 6, the strength of the acids formed increasing with the valence.

H_2S is decomposed by free I, with the formation of free S and HI. Both H_2S and H_2SO_3 are oxidized to H_2SO_4 by $KMnO_4$. These reactions are used for titration.

Hexavalent and tetravalent S are reduced to divalence by H at red heat. Elemental S and the lower valences are oxidized to hexavalence by Br, and by O in the presence of catalysers. Divalent and tetravalent S are oxidized to hexavalence by a mixture of three parts HNO_3 and one part HCl.

BaSO_4 is the compound most commonly weighed.

Only the sulfates of the stronger bases are involatile on ignition in air, but sulfides of these bases are partly converted to sulfates on ignition.

Phosphorus.—Following N in the series, P is more decidedly acid in its tendencies though its acidity is not so powerful. Phosphonium, the homolog of ammonium, is too unstable to be of analytical importance.

The valences are 3 and 5. The trivalent forms are unstable, and are not used in the assay of P, though hypophosphorous acid HPH_2O_2 is a valuable reducing agent.

For purposes of its assay, P is oxidized to the pentavalent form, if not so already, KMnO_4 being a convenient reagent for that purpose, in acid solution.

P is separated as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ and weighed as $\text{Mg}_2\text{P}_2\text{O}_7$. It is also weighed as the "yellow precipitate," ammonium phospho-molybdate, $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 3\text{H}_2\text{O}$, and weighed as such or titrated, either by alkali or by reducing the Mo.

Phosphine is the only volatile compound of importance, and its formation is prevented by avoiding the evolution of H during the decomposition of the sample.

Phosphates are occluded in and also absorbed by metastannic acid, and are occluded in hydrates, particularly those of Fe and Al. This property is used for the concentration of P in the sample, by the separation of elements not included in those precipitates.

Tungsten.—Coming near the bottom of the series, the properties of the series are so weakened in W that it is known more by its individual peculiarities.

Its valences are 2, 4, 5 and 6, of which the last is the most stable. In its divalent and tetravalent forms it is a weak base, unstable, and neither valence is formed in analysis.

In HCl solution Zn reduces W to blue WCl_5 , unstable, but used as a test.

With O hexavalent W forms the stable WO_3 and the acid H_2WO_4 .

Oxidation and reduction are not used in its assay.

Like silica, the acid is soluble, unless dehydrated. Its most insoluble compound is precipitated from acid solution by cinchonine hydrochloride. It is weighed as WO_3 ; color, yellow.

The sulfide is formed only by the acidulation of the alkaline sulfide solution. Tartaric acid prevents its formation.

Tungstates are soluble in alkalies, and are not occluded in hydrate precipitates.

W is not volatile from solution, nor on ignition, but may be volatilized by heating the oxide in CCl_4 , forming WCl_6 .

Fluorine.—This is the lightest of the halogens, and decidedly different from the others. Its valence is 1, and it is not reducible by analytical methods.

Its characteristic compound is HF , a moderately strong acid and a powerful solvent.

F is precipitated and weighed as CaF_2 , which is slightly soluble in water.

SiF_4 is a gas, and by means of it F may be determined by difference, or by distillation.

Chlorine.—The valences of Cl are 1, 5 and 7, all of which are stable, and some unstable compounds which suggest other valences between 1 and 5. The higher valences are not produced as an analytical procedure, differential reduction being used in the determination of the various ions.

HCl is typical of the monovalent form; a strong acid and a solvent.

Free Cl, since it has oxidizing power, is brought to monovalence by reducing action, all reducing agents reacting with it.

Chlorates, from HClO_3 , the pentavalent form, are reduced by ferrous salts and H_2SO_3 , which do not reduce perchlorates.

Perchlorates, from HClO_4 , are reduced in acid solution by metallic Zn, which also reduces chlorates.

AgCl is insoluble in dilute acids, and soluble in NH_4OH or $\text{Na}_2\text{S}_2\text{O}_3$ solution. Cl is precipitated as AgCl and weighed as such or as Ag. AgCl is involatile on heating to fusion.

Bromine.—Br has the same valences as Cl, and forms homologous compounds, but its affinities are lower and it is easily displaced from its compounds by Cl.

As it is precipitated as AgBr and can be weighed both as such and as Ag , Cl and Br may be determined together by calculation.

Iodine.— I follows Br in the series, with higher boiling points, and weaker affinities.

Hydriodic acid, HI , is oxidized to involatile iodic acid, HIO_3 , by CrO_3 , while hydrochloric and hydrobromic acid are oxidized to gaseous Cl and Br . This permits the differential determination of all three halogens together.

Arsenic.—This element, the most electro-negative of those classed as metals and found in alloys, carries to extremes many properties which it shares with other metals. Its acid properties are most pronounced, its compounds are with the exception of Hg the most volatile, its sulfides are least soluble in acids and most soluble in alkalies, and it has the least tendency to electro-deposition.

Its valences are 3 and 5. Both conditions are stable on exposure to air. In hot concentrated HCl , AsCl_5 is readily reduced to AsCl_3 by the presence of ferrous salts, and in concentrated and more dilute acid by cuprous salts, H_3PO_2 and H_2SO_3 . Organic matter in fuming H_2SO_4 also reduces pentavalent As .

Arsenic solutions in presence of acid are reduced by iodides, setting free I .

Arsenious compounds are oxidized by HNO_3 , by free Cl and by free I in neutral solution, but the last has but slight effect in acid solution.

As is precipitated and weighed as As_2S_3 . It is also precipitated as $\text{MgNH}_4\text{AsO}_4$ and weighed as $\text{Mg}_2\text{As}_2\text{O}_7$.

AsCl_3 is volatile with boiling HCl , 50 per cent or stronger.

AsH_3 , gaseous, is formed by nascent H on the solution of metals in acid, in presence of As in any soluble form.

All compounds of As with volatile elements are volatile on ignition.

As is readily precipitated as As_2S_3 from its trivalent salts in acid of any strength. Its color is canary yellow. It is easily soluble in all alkalies, even $(\text{NH}_4)_2\text{CO}_3$, which last serves to separate it from other members of its group.

As_2S_5 is slowly precipitated, mixed with As_2S_3 , from pentavalent solutions in dilute acids. From HCl equal to 75 per cent or more of its ordinary reagent strength, 1.19 specific gravity., As_2S_5 is completely precipitated, making a separation from all other basic ions except Se . Precipitated As_2S_5 has the same properties as As_2S_3 except weight.

As is precipitated by ammonium molybdate.

When alloys containing As with Sn or Sb are decomposed with HNO_3 , the insoluble residue contains all or part of the As .

$\text{Fe}(\text{OH})_3$ and several other hydrates, if formed in presence of arsenic solution, will carry all or part of it into insoluble precipitate.

Antimony.—The properties of Sb are similar to its serial antecedent As , modified in the direction of the electro-positive pole. It has also much in common with its neighbor Sn .

Its valences are 3 and 5. Like Sn , it forms an apparently tetravalent oxide, which may be a combination of its regular valences.

Trivalent Sb acts as a base. Sb_2O_3 reacts with strong bases to form antimonites, such as NaSbO_2 .

Pentavalent Sb acts as a base. Sb_2O_5 has decidedly acid properties, as HSbO_3 and $\text{H}_4\text{Sb}_2\text{O}_7$.

SbCl_5 is reduced to SbCl_3 by ferrous salts in strong HCl , and in strong or weak acids by cuprous salts, H_3PO_2 and by H_2SO_3 . The last acts best in warm solutions, on account of its volatility.

Antimonic solutions in presence of acid are reduced by iodides, setting free I .

Antimonious compounds are oxidized by HNO_3 , by free Cl and by free I in neutral solution.

Small quantities of Sb are precipitated as Sb_2S_3 and weighed as Sb_2O_4 . It is also precipitated and weighed as $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$.

SbCl_3 is volatile with HCl at a temperature approaching that of fuming H_2SO_4 .

SbH_3 , gaseous, is formed by the action of nascent H on solutions of Sb . As metallic Sb is insoluble in HCl , and is reprecipitated during solution of alloys in that acid, the danger of loss as SbH_3 is slight.

Antimonious compounds are volatile at ignition temperatures. By thorough oxidation Sb_2O_4 is produced, which may be ignited without loss.

Sb_2S_3 and Sb_2S_5 are so nearly alike in all their properties as to be indistinguishable. Their color is red with a slight tinge of yellow. They are precipitated in HCl of all concentrations up to 30 per cent of the reagent, cold or 16 per cent hot, but in the higher concentrations are unstable on exposure to air. They are soluble in hydrates and sulfides of Na and K , and in sulfides of NH_4 .

Sb salts in solution are easily hydrolyzed, considerable excess of acid being necessary to keep them in solution. Tartaric acid prevents hydrolysis, and permits the formation of neutral and alkaline solutions. In this respect Sb resembles its serial succedent, Bi .

Though the hydrates are soluble in excess of alkali, they are made insoluble by occlusion in other hydrates, such as $\text{Fe}(\text{OH})_3$.

PbSO_4 will occlude some Sb if the latter is present in more than traces in the H_2SO_4 solution.

Tin.— Sn resembles analytically none of the common elements in its series, but has much in common with its lateral neighbor Sb .

Pb , Ni and Fe , though electro-positive to Sn , are unable to precipitate it electrolytically, Zn being the first metal having that property.

The valences of Sn are 2 and 4.

Divalent Sn acts as a base and its oxide forms stannites such as Na_2SnO_2 in excess of alkali.

Tetravalent Sn acts as a base. Its oxide forms stannic acid, H_2SnO_3 and metastannic acid, $\text{H}_{10}\text{Sn}_5\text{O}_{15}$.

SnCl_4 is reduced to SnCl_2 in HCl by the solution of metallic Pb , Fe or Ni . Free I oxidizes stannous solutions to stannic.

Sn is converted to metastannic acid by action of HNO_3 on the metal, and is precipitated quantitatively as SnS_2 . Both are weighed as SnO_2 .

SnCl_4 in absence of H_2O is highly volatile, and its volatility is considerable on the evaporation of chloride solutions nearly or quite to dryness on the waterbath, or on the evaporation of mixed HCl and H_2SO_4 solutions to the expulsion of H_2O . Prolonged boiling in concentrated HCl entails some loss, but this is negligible in analytical work unless the solution boils almost dry.

Sn compounds may be partly volatilized by the reducing action of C if ignited with insufficient air.

SnS_2 may be completely precipitated from HCl solutions as strong as 16 per cent cold or 8 per cent hot. The presence of $\text{H}_2\text{C}_2\text{O}_4$ prevents its precipitation, but not that of SnS .

SnS_2 is readily soluble in hydrates and sulfides of Na and K , and in sulfides of NH_4 . SnS is not soluble, except by oxidation.

SnS_2 is brownish yellow when collected, though it may be white when first precipitated from $\text{HC}_2\text{H}_3\text{O}_2$. SnS is greenish brown, and more dense than SnS_2 , which is slimy.

Sn salts have a marked tendency to hydrolysis. Its hydrates are too slimy to filter alone.

Occluded with other hydrates, Sn may be precipitated and filtered.

Sn has no tendency to combination with PbSO_4 , as is the case with Sb .

Selenium.— Se follows S in the series, and its compounds are similar, but its properties incline more to those of a metal. It is strongly electro-negative, and easily reduced electrolytically.

Its valences are 2, 4 and 6. The higher valence is unstable, H_2SeO_4 being reduced to H_2SeO_3 by boiling with HCl . H_2SO_3 reduces H_2SeO_3 to Se . H_2S produces an unstable sulfide, SeS , which reduces quickly, but as the element remains insoluble in acid, and dissolves in alkaline polysulfides, Se is included in the H_2S group.

Se is precipitated and weighed as the element. It may be completely reduced and precipitated in HCl as strong as 80 per cent. Seventy per cent is customary, which gives a separation from Te . Se is red when precipitated, turning to black on heating. Metallic Se is volatile on ignition.

The chlorides of Se are more or less volatile, and special precautions need to be taken during analysis to prevent loss. On this account assays of Se should be made on separate samples. Se can be separated by volatilization from elements having involatile chlorides.

Like its neighbor As, Se is occluded in hydrates when in solution at the time of precipitation.

Tellurium.—Te, following Se in the series, resembles it closely in all its compounds and reactions. The same reagents oxidize and reduce it.

It is precipitated and weighed as the element. It is more soluble than Se, 60 per cent HCl preventing its precipitation by H_2SO_3 . From 10 per cent to 15 per cent is the customary strength for precipitation. The precipitated element is black.

The chlorides of Te are volatile, giving the same uses and dangers as those of Se. It follows Se in reactions with H_2S and in occlusion.

Molybdenum.—With atomic weight between Se and Te, but on another branch of the same series, Mo is decidedly different from them.

Its valences are 2, 3, 4, 5 and 6. Hexavalent Mo forms molybdic acid, H_2MoO_4 , and many addition and substitution products of MoO_3 . In the other valences Mo is basic. It is not reduced to metal in the wet way, but its reduction by Zn in acid solution to the trivalent form, and oxidation to the hexavalent by KMnO_4 , is the basis of the best method of assay. By HI it is reduced to pentavalence with liberation of I. Mo is not volatile from solution, but ignition is difficult.

H_2S precipitates insoluble MoS_3 from acid solution, but during precipitation reduces a part of the solution below hexavalence to a blue solution of unknown valence near 5, which forms no sulfide. The sulfide is soluble in alkaline sulfides, giving a red color.

There are a number of insoluble molybdates, the most convenient of which is PbMoO_4 , which is precipitated in $\text{HC}_2\text{H}_3\text{O}_2$ solution. The solubility of hexavalent Mo in NH_4OH and its

freedom from occlusion in precipitated hydrates gives the best method of separating it from the other members of its group.

Silver.—Ag is unique among the heavier metals in having no higher valence than 1.

It is classed among the noble metals because its most stable form is the metallic, most of its compounds being reduced by heat alone. From solution it is reduced to metal by such reagents as FeSO_4 .

It is precipitated and weighed as AgCl , and in the fire assay as metallic Ag.

It forms no volatile compounds.

Ag_2S is easily precipitated and insoluble in both acids and alkalies.

The solubility of its chloride in NH_4OH and its insolubility in dilute HNO_3 serve to distinguish it.

Mercury.—Hg has hardly any resemblance to the other elements of its series. It has two valences while they have one. Its low melting point and the volatility of all its compounds distinguish it from all others. Electrically it is regular, being next to, and negative to H.

The valences of Hg are 1 and 2. It is stable in both valences, though some of its compounds have a tendency to decompose and reduce to Hg. Change of valence is used in methods for assaying salts of Hg.

Hg is weighed generally as Hg, though the sulfide HgS may be used. All compounds of Hg, without exception are volatile at moderate ignition temperatures, but volatility from solution is not a source of loss.

HgS , the only sulfide, is less soluble in acid than any other member of its sub-group, and it is insoluble in alkalies except where the formation of double sulfides of Na or K is possible.

HgCl is of interest, as by its precipitation, insoluble in acids, and insoluble but turning black by reduction in NH_4OH , monovalent Hg may be identified and separated.

The reduction of Hg compounds to metal by heating in contact with Fe and its distillation form the basis of most assay and metallurgical work with Hg.

Lead.—In the periodic system Pb is far removed from its analytical associates, except its neighbor Bi. In the Lothar Meyer table its characteristics are more clearly indicated.

Electro-positive to H and several other metals, the character of Pb in this respect is masked by the insolubility of its chloride and sulfate, and by its ability to precipitate on the anode as PbO_2 .

Pb has only one valence, 2, in solution, but may be tetravalent as oxide. Its reduction, as such, to divalence, is easy, interference coming from the formation of insoluble compounds. The tendency of PbO_2 to reduce is shown by its ability to oxidize Mn to permanganic acid. Titration methods are based on this reduction.

Pb is not volatile from solution, but Pb and PbO are easily volatile on ignition, and other compounds are reduced by heating with C, so ignition of precipitates on paper is difficult.

Pb is precipitated and weighed as PbSO_4 , PbCrO_4 and PbO_2 .

PbS is precipitated by H_2S from acid and alkaline solutions, black. The allowable strength of HNO_3 is 5 per cent. In HCl the acidity should not be more than 4 per cent at 40° or 2 per cent at 60° . Above these limits the reddish brown chlor-sulfide, a mixed chloride and sulfide, may be precipitated, with danger of incomplete precipitation. On this account PbS from HCl should be washed with solution containing H_2S . The sulfide is insoluble in alkalies and alkaline sulfides.

The most soluble Pb compound is the acetate, but this requires an excess of $\text{HC}_2\text{H}_3\text{O}_2$ to prevent hydrolysis.

In accordance with its electrolytic position, Pb is dissolved in HCl with evolution of H, but heat and sufficient dilution are necessary to prevent the chloride from occluding and protecting the undecomposed metal. The solubility of PbCl_2 in acid solutions at room temperature is, roughly, as follows:

% HCl	0	2.5	5	10	15	20	30	100
% Pb	0.63	0.08	0.05	0.06	0.08	0.09	0.20	15

PbSO_4 formed by boiling H_2SO_4 solutions to fumes of SO_3 will occlude Bi, Sb, Ba and Sr, if those elements are present in quantity more than a few milligrams, causing some Pb to re-

main insoluble in $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$. CaSO_4 may remain undissolved in dilute H_2SO_4 , dissolve in the acetate, and be occluded in the PbCrO_4 . Methods of analysis must provide for these possibilities.

The easy fusibility of PbO is a distinguishing characteristic of Pb .

Bismuth.— Bi shows the regular characters of its place in the series, which increases in the basic tendency with the atomic weight. In the electro-potential series it is positive to Cu and H , and next to Cu , to the detriment of the Cu assay.

Bi has one valence, 3. In the wet way its hydrate is reduced to metal by alkaline stannites, such as Na_2SnO_2 .

Bi is precipitated as carbonate and weighed as oxide. It is precipitated and weighed more commonly as BiOCl , formed by hydrolysis of the chloride.

Bi is precipitated from HCl , HNO_3 and H_2SO_4 as strong as 5 per cent by H_2S . From HCl the precipitate is not easily washed, tending to run through the filter.

Bi_2S_3 is insoluble in alkalis, but is difficult to wash except with NH_4S_x . It is precipitated in good form from ammoniacal tartrate or cyanide solutions. The tartrate gives a good separation from Te , and the cyanide from Cu .

The carbonate is completely precipitated with difficulty from $(\text{NH}_4)_2\text{CO}_3$ solution. It is useful as a separation from occluded sulfates.

The oxychloride is precipitated easily by diluting a concentrated slightly acid solution of the chloride. It tends to occlude TeO_3 and SO_3 which must be removed before the precipitation.

The occlusion of Bi by PbSO_4 has been mentioned.

Copper.—Being followed in the series by noble metals, Cu tends to stability in metallic form. One step more positive than H , Cu is the most adaptable to electrodeposition of all the elements.

Cu has two valences, 1 and 2, of which the divalent form is more stable. Reduction is produced by such reagents as H_2SO_3 . This is useful in separations, and some titration methods are based on it.

Cu forms many weighable compounds, of which the oxide, precipitated as such or formed by the ignition of the sulfide, is most commonly used. The electrolytically precipitated metal is the best gravimetric form.

Cu compounds are not volatile from solution, but Cu_2Cl_2 is volatile on ignition; for which reason Cu precipitates containing traces of chlorides must be heated slowly and well roasted before heating to redness.

CuS is precipitated from acid solutions. The allowable strength of HCl is 16 per cent hot and 33 per cent cold; H_2SO_4 as much as 15 per cent, and HNO_3 limited only by the decomposition of H_2S . The sulfide is ordinarily black, but when precipitated from dilute HNO_3 it appears brown.

The sulfide is slightly soluble in alkaline polysulfides, but particularly so in NH_4S_x .

CuCl_2 and $\text{Cu}(\text{NO}_3)_2$ are highly soluble in their acids, but CuSO_4 is much less so. Ten grams of Cu, dissolved and heated with 20 cc. of H_2SO_4 to expel other acids, must be diluted to 135 cc. to prevent crystallization.

The blue solution produced by dissolving $\text{Cu}(\text{OH})_2$ in excess of NH_4OH is of value as a basis for color comparison. This solubility of the hydrate is used to separate Cu from Fe and from the many elements which are occluded by $\text{Fe}(\text{OH})_3$, such as As, Sb, Se, Te and Bi.

Cadmium.—Cadmium belongs to a series of low melting and boiling points, culminating with Hg. It closely resembles its antecedent Zn, differing in slight degree in most of its properties. It is electro-positive to H, but not so much so as to make deposition difficult.

Its valence is 2. It is not reduced to metal in the wet way. On ignition with paper it is reduced and may be volatilized unless careful roasting is practiced. Like Zn, the metal is much more volatile than the oxide.

The sulfide is the only insoluble compound of importance. It can be completely precipitated from H_2SO_4 solution as strong

as 5 per cent, the presence of $(\text{NH}_4)_2\text{SO}_4$ assisting to bring down small amounts. HCl or HNO_3 may also be used if the acidity is not too high.

The sulfide is also produced from NH_4OH solution, or ammoniacal cyanide, and is insoluble in alkalis. Its yellow color is characteristic in its analytical position.

The sulfate can be ignited without loss, by evaporating the solution.

Zn is likely to be occluded in the CdS precipitate, and two or more precipitations are necessary to separate large quantities of it.

Aluminium.—Though there are several elements which show many of the analytical properties of Al, so that it has no characteristic reactions by ordinary reagents, the other elements are either rare or easily separated.

Complete separation from the other elements and the appearance of its hydrate make the test ordinarily depended upon for its identification.

While appearing generally as a basic ion, Al has marked acid tendencies, forming soluble aluminates with alkalis, such as NaAlO_2 . Metallic Al dissolves in NaOH or KOH with evolution of H.

Its valence is 3. It is not reduced to metal in the wet way.

The chloride and other halogen compounds of Al are volatile on ignition. For this reason Al should be precipitated from a sulfate or nitrate solution preparatory to ignition.

Al_2S_3 is decomposed by water, the hydrate being completely precipitated by NH_4S_x , in the absence of free NH_4OH .

The hydrate is precipitated in a neutral solution containing some ammonium salts as a coagulant. It is less soluble in a slight excess of acid, such as is formed by boiling ammonium salts, than in excess NH_4OH .

Al is precipitated and weighed as the phosphate, AlPO_4 . It is precipitated as the hydrate, $\text{Al}(\text{OH})_3$ and weighed as Al_2O_3 . The highest blast temperature is necessary for its complete dehydration.

$\text{Al}(\text{OH})_3$ occludes P_2O_5 when present, forming the phosphate.

Al forms no colored compounds with ordinary reagents in the wet way.

Chromium.—Cr resembles Mo, its succedent in the periodic series, in having a variety of colored precipitates and solutions, but has not the same multiplicity of valences.

Cr has two stable valences, 3 and 6. Trivalent Cr has the same behavior as Al, forming hydrates in neutral solutions, soluble chromites with excess of alkalis, and acting as a basic ion in acid solutions.

Hexavalent Cr forms the acids H_2CrO_4 and $\text{H}_2\text{Cr}_2\text{O}_7$, which exist only in solution, forming stable salts. Cr is reduced to trivalence by boiling in HCl , a property which it shares with its succedents Se and Te and its neighbor V. Hexavalent Cr is also reduced in acid solution by peroxides, through the formation of unstable perchromates, which decompose to the trivalent chromic compounds.

In the acid solution Cr is not easily oxidized to hexavalence, KMnO_4 having no effect, though strong aqua regia does it partially, but in alkaline solution peroxides make the change completely.

The reduction of Cr from hexavalence to trivalence is the basis of accurate titration methods.

Cr is weighed as PbCrO_4 and as Cr_2O_3 .

Chromates and vanadates interfere through the similarity of their properties.

Uranium.—U has marked resemblances to its antecedent Cr, showing several valences, colored solutions and salts, and both acid and basic properties.

U has one stable valence, 6. In this valence it forms basic compounds containing UO_2 , called uranyl, which was once thought to be the element. In reduction reactions a uranyl salt, such as UO_2SO_4 , behaves in the same way that $\text{U}(\text{SO}_3)_3$ would.

Tetravalent U in solution is sufficiently stable for titration purposes. Trivalent U is extremely unstable, being rapidly oxidized to tetravalence on exposure in solution to air. Zinc in acid reduces U partly to tetravalence and partly to trivalence.

Hexavalent U salts and solutions are yellow. Trivalent U solutions are olive green, and tetravalent solutions grass green. U is oxidized to hexavalence in acid solution by KMnO_4 . Titration methods are used.

There are no troublesome volatile U compounds.

UO_2S is precipitated completely by NH_4SH . It is soluble in acids.

NH_4OH precipitates $(\text{NH}_4)_2\text{U}_2\text{O}_7$, which is ignited and weighed as U_3O_8 .

In presence of phosphates or vanadates UO_2HPO_4 or $\text{UO}_2(\text{VO}_4)_2$ are precipitated on neutralization, instead of the uranate. The presence of an excess of phosphates will prevent the formation of the vanadate.

Alkaline carbonates produce soluble U compounds, permitting easy separations from Fe and Al.

The reddish brown color produced by $\text{K}_4\text{Fe}(\text{CN})_6$ with U salts provides a good qualitative test for U, as well as a valuable indicator for the titration of Zn.

Vanadium.—V has some resemblance to its neighbor Cr, but is otherwise unique.

It has one stable valence, 5, with yellow or colorless solutions, and one slightly less so, with blue solutions. An unstable pervanadic acid produced by H_2O_2 is intense red, giving a characteristic test for V.

Hexavalent V is reduced to tetravalence by H_2S , H_2SO_3 , by heating with HCl and by electrolysis. Zn reduces it below tetravalence, and with care the trivalent condition can be completely produced. KMnO_4 oxidizes it to pentavalence. Several titration methods are used, with KMnO_4 .

Pentavalent V with O forms vanadic acid, giving such salts as PbVO_4 . It is soluble in alkalis, but forms several insoluble salts, particularly with Pb and Hg.

Tetravalent V forms basic salts with O called vanadyl salts, of which $\text{V}_2\text{O}_2\text{Cl}_4$ is a type.

V is precipitated as Hg_2VO_4 and weighed as V_2O_5 , but titration methods are generally relied on.

The occlusion of V with $(\text{NH}_4)_2\text{U}_2\text{O}_7$ is important in analysis. It is also occluded partially in $\text{Fe}(\text{OH})_3$.

Iron.—Classed in the triads, Fe has but slight resemblance to its mates. Standing between Ni and Zn in the electro-potential series, it displaces H from acids, and is reduced to metal electrolytically.

Fe has two valences, 2 and 3, both of which are basic in character.

Trivalent Fe is reduced by H_2S and by H_2SO_3 , but not by HCl. Divalent Fe is oxidized by KMnO_4 but not by I. Titration is the most accurate method of assaying Fe.

Black FeS is precipitated by alkaline sulfides from both ferrous and ferric solutions. It is soluble in 10 per cent H_2SO_4 .

$\text{Fe}(\text{OH})_3$ is precipitated completely by excess of NH_4OH , and is weighed as Fe_2O_3 .

FeCl_3 is volatile at temperatures slightly above boiling, such as are obtained by baking an insoluble residue. Excess H_2SO_4 prevents this loss. Precipitates should not be made from the chloride solution for ignition.

P and V, which remain in the filtrate from the H_2S group, are occluded in $\text{Fe}(\text{OH})_3$, P completely and V partially.

KCNS is useful to show whether a solution which is being reduced still contains any trivalent Fe, and $\text{K}_3\text{Fe}(\text{CN})_6$ to show whether any divalent Fe is present, but neither is useful in the course of analysis to show whether Fe is present. Many solid reagents contain traces of Fe, and H_2S , unless carefully washed, carries it in the spray from the generator. By the time Fe has been reached in the analysis, therefore, a trace has generally been introduced, and only quantitative comparison with a blank determination is a reliable test for small amounts of Fe. The color tests are valuable only when they can be used on the sample without preliminary separations.

Titanium.—Ti is without close resemblance among the commoner elements, its succedents being rare. Ti itself is far from rare, being found in traces in most rocks.

Its valences are 3 and 4, of which the latter is stable, and the former highly unstable. Tetravalent Ti is reduced by Zn in

acid solution, but must be protected from air to prevent rapid oxidation. It is not reduced by H_2SO_3 or H_2S . Trivalent Ti solution is violet in color. Tetravalent Ti is colorless. In acid solution, H_2O_2 produces a higher valence with an intense orange red color, showing yellow when dilute. This reaction is prevented by the presence of HF.

In ordinary analysis, Ti remains with Fe, except that in presence of P_2O_5 it forms a residue insoluble in acid, which is decomposed by fusion with Na_2CO_3 , and filtering the alkaline solution.

When Fe is reduced in the ordinary way, Ti in small quantities does not interfere. After titrating the Fe with KMnO_4 , Ti up to 0.005 gram is estimated by color comparison with H_2O_2 , and counted as TiO_2 among the combined oxides from the ignition of the NH_4OH precipitate.

Manganese.—Mn is an element of many colors and valences, like its neighbors of Group 6 in the periodic system. Its succedents in its own series are missing.

Mn has three valences of interest in analysis, 2, 4 and 7. It is stable in all three forms.

Manganous salts, such as MnSO_4 , are slightly pink.

MnO_2 is almost black.

Permanganates, such as KMnO_4 , are deep purple, showing red when dilute.

Reducing agents in acid solution such as FeSO_4 , $\text{H}_2\text{C}_2\text{O}_4$, H_2O_2 and HCl reduce both the higher forms to divalence. MnO_2 is formed by the oxidation of manganous salts, as a precipitate. In neutral solution, heptavalent and divalent Mn combine to form MnO_2 . Accurate titration methods are based on these reactions.

Mn is precipitated as $\text{NH}_4\text{MnPO}_4 \cdot \text{H}_2\text{O}$ and weighed as $\text{Mn}_2\text{P}_2\text{O}_7$.

Volatility is not a source of loss in the Mn assay.

MnS is precipitated in alkaline solution. A bare trace of acid will dissolve it.

A precipitate approaching MnO_2 in composition is produced by several oxidizing agents, particularly $(\text{NH}_4)_2\text{S}_2\text{O}_8$, in excess

of NH_4OH , which makes a good separation for small quantities. It is ignited and weighed as Mn_3O_4 .

Zinc.—Zn and Cd, its succedent in the series, are much alike, differing principally in the color and solubility of their compounds.

Zn is the most positive of the metals which can be electro-deposited under laboratory conditions, its properties approaching those of an alkali though it forms soluble zincates in excess of KOH or NaOH, metallic Zn dissolving with evolution of H.

Its valence is 2. It is not reduced by reagents.

It is one of the most volatile of the metals, but its oxide and all other compounds except the halides are involatile on ignition.

Zn is precipitated as ZnS and weighed as ZnO . With the utmost precautions, some S is likely to remain as ZnSO_4 .

ZnS is the only white sulfide of the common elements. It is precipitable in a higher acidity than others of the ammonium sulfide group, as much as 0.1 normal H_2SO_4 , or 0.2 per cent of the reagent, including the acid combined with the Zn, being permissible.¹

Zn is also precipitated completely in solutions containing sulfates with not more than 0.1 per cent excess of HCl, and in $\text{HC}_2\text{H}_3\text{O}_2$ as strong as 10 per cent. These acid precipitations are useful as separations from Ni and Co.

Nickel and Cobalt.—Ni and Co resemble Cu so closely in many respects that it would seem that they should occupy the vacant space in the zero group.

Many of their reactions are identical, and will be described together.

Electrolytically they are negative to Fe and Zn, and are easily deposited from alkaline solutions.

Both are divalent in solution, and decidedly basic in their tendencies.

Ni solutions are green in acid and blue in excess of NH_4OH , while Co forms rose pink solutions. When both are present, the colors may neutralize each other, giving an almost colorless solution.

¹G. Weiss. Cf Scott; "Standard Methods of Chemical Analysis."

Volatile compounds give no trouble.

Both are electrodeposited and weighed as metal, or as sulfide and weighed as oxide.

Their sulfides are peculiar in that a slight excess of mineral acid will prevent their precipitation, but the precipitate is very slightly soluble in acids, except by decomposition of the sulfide. The sulfides are black, and are precipitated from NH_4OH solution and coagulated by adding a slight excess of $\text{HC}_2\text{H}_3\text{O}_2$ after precipitation, for better filtration.

Ni is precipitated with di-methyl glyoxime and weighed as $\text{NiC}_8\text{H}_{14}\text{N}_4\text{O}_4$, this being a separation from Co and Zn.

Co is precipitated by nitroso-beta-naphthol, ignited and weighed as Co_3O_4 . This is a separation from Ni and several other elements.

Calcium.—Ca is one of the strongest bases, almost equal to the alkalis, its alkalinity being reduced by the slight solubility of its oxide.

Its valence is 2. It is not reduced to metal under laboratory conditions.

Its halides are volatile on ignition, but in combination with O it is highly involatile.

Its sulfide is soluble in water. Alkaline sulfides are therefore better media than ammonia for separating Ca from the ammonium sulfide group.

Ca is ordinarily precipitated as $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and weighed as CaO, or the oxalate titrated with KMnO_4 .

The oxalate precipitate tends to occlude Mg.

Magnesium.—Mg is almost as strong a base as Ca, but its oxide is almost insoluble in water, giving it slight alkaline properties.

Its valence is 2, and it is not reducible.

Its salts are generally more soluble than those of Ca. As both are separated together from most other bases, only the separation of Mg from Ca need be considered.

None of its compounds are volatile.

Mg is precipitated as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ and weighed as $\text{Mg}_2\text{P}_2\text{O}_7$.

Barium.—Ba is a base and an alkali of about the same strength as Ca.

Its valence is 2, and it is not reducible.

Its solubility during separations is about the same as that of Ca, except that the sulfate and the carbonate are insoluble. Since H_2S always produces some H_2SO_4 , BaSO_4 will separate all through the analysis, if it is not separated at the start. As it rarely occurs in alloys, and generally as the sulfate in minerals, it is generally found in the residue after the expulsion of SiF_4 .

Ba is precipitated and weighed as BaSO_4 . BaSO_4 is decomposed by fusion with Na_2CO_3 , BaCO_3 being insoluble in water.

Strontium.—Sr has most of the general characteristics of Ca and Ba, standing between the two as to the solubility of the sulfate. In the absence of Ba, Sr will be found in the oxalate precipitate with Ca. Special methods are used for their separation.

Potassium.—K has a valence of 1, is not reduced to metal by laboratory methods, and is not separated in the regular course of analysis.

Special methods are used to separate other elements except the other alkalis, after which K is precipitated and weighed as chloroplatinate, K_2PtCl_6 , or perchlorate, KClO_4 .

The purple flame color of K is distinctive.

All the compounds of K are soluble in water, even those used for its assay, which are separated from the corresponding compounds of Na by dissolving the latter in alcohol.

Sodium.—Na is similar to K, except that the chloroplatinate and the perchlorate are soluble in both water and alcohol, but the pyroantimonate, $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot \text{H}_2\text{O}$ is very slightly soluble in water and insoluble in a mixture of half water and half alcohol.

The flame test for Na, an intense yellow, is too delicate to be useful, since almost every substance will give the test. It may be used, however, to identify a sodium compound if a minute portion is dissolved in pure water and a drop gives a strong color.

Sodium is ordinarily weighed as chloride, any K or Li being afterward determined and subtracted.

Lithium.—Li is distinguished principally from the other alkalies by its intense carmine red flame color. Its chloride is soluble in amyl alcohol, while the chlorides of Na and K are not. The Gooch separation is based on this.²

² Scott, "Standard Methods of Chemical Analysis."

CHAPTER IV

REAGENTS

Ammonia Water.—The ordinary solution has a specific gravity of 0.9 containing 28.5 per cent of NH_3 , which makes it about 15 normal. Owing to its volatility, the bottle on the shelf may be 10 per cent weaker.

NH_4OH is a much weaker base than NaOH or KOH . Ammonium salts lose NH_3 on boiling and cause the solution to become acid.

They may be removed from a solution without evaporation and ignition by warming with alternate additions of HNO_3 , and HCl , which decomposes NH_4OH to N and H_2O .

Ammonium salts are the best coagulants for precipitates, since they are easily soluble in both acid and alkaline solutions and cause less trouble from precipitation than do the fixed alkalies. The convenience of having an alkali supplied in liquid form, from which salts can be made by adding acid, gives ammonia the preference over the fixed alkalies in most analytical operations. It is often of advantage to be able to boil off the excess of alkali, which can be done only with ammonia. Thirty minutes boiling is sufficient to bring to neutrality a solution having a strong excess of NH_4OH .

By saturating NH_4OH with H_2S , NH_4SH is obtained. By oxidation of the air or by dissolving free S this is converted to polysulfide known as NH_4S_x . NH_4SH is colorless. As a precipitant, or a solvent for sulfides it is to be preferred to NH_4S_x , as it contains only the ions which enter into the reaction. During the reaction some yellow polysulfide is formed, so the advantages of both forms are generally obtained by the use of fresh NH_4SH alone. The polysulfide has the advantage that it will dissolve, slowly and imperfectly, SnS . SnS , however should never be precipitated, except as a curiosity. NH_4S_x is a better coagulant for sulfides than NH_4SH .

When polysulfides of the fixed alkalies are treated with ammonium salts NH_4S_x is formed, but the capacity of NH_4 for S

is less than that of Na or K. To prevent precipitation of S it is necessary to add some NH_4OH .

Sodium and Potassium Salts.—Na salts being cheaper than K salts are preferred where they can be used. Many of them are more hygroscopic than the corresponding K salts.

NaOH takes up water from the air more readily than KOH, and is less convenient to handle. NaNO_3 and $\text{Na}_2\text{S}_2\text{O}_7$ are not used for fusions on account of their taking up water.

Na_2CO_3 is the most used reagent for alkaline fusions, since it can be used in platinum. The addition of even a small proportion of K_2CO_3 notably lowers the melting point.

NaSH is more easily obtained than KSH, and is therefore used as a solvent for sulfides, but KSH, made by saturating KOH with H_2S , is preferable because Na makes an insoluble antimonate and K does not.

KOH is as good a solvent for sulfides as KSH, but some KSH should be used with it to convert such compounds as chloresulfides into normal sulfides and keep the metallic elements in their analytical places.

When K salts are used as coagulants they must be in a concentration of at least 5 per cent to be effective. Na salts should be in the same molecular concentration, though with a proportionately less percentage.

Stock Alkali Solution.—Make a solution containing 5 per cent KOH and 5 per cent of K_2SO_4 and pass H_2S long enough to saturate about 1/10 of the KOH. If K_2SO_4 is not on the shelf, use 36 grams of $\text{K}_2\text{S}_2\text{O}_7$ and 66 grams of KOH per liter, which will give the same solution. Let the solution stand for several days to settle out impurities, decant and use to dissolve sulfides.

This solution is almost as strong as a paper filter will bear. If it is used as a washing solution when a precipitate is inclined to run through the filter, it must not be diluted, as at least this much neutral salt is needed if it is to be of any use as a coagulant for precipitates.

Sulfuric Acid.—Reagent H_2SO_4 has a specific gravity of about 1.84, 95.6 per cent H_2SO_4 , 1,759 grams H_2SO_4 per liter and 35.9 normal.

In dilute solution it has the acidity of a monobasic acid, being ionized as $\text{H}-\text{HSO}_4$, so that its solvent action is half what its normal value would indicate. In neutralization and precipitation it forms normal salts in most cases, both of its H ions being displaced.

In concentrated solution it is a more powerful solvent for many elements than when more dilute. When heated it is also an oxidizing agent, decomposing with metals and converting them to sulfates.

Much of its action depends on its strong affinity for H_2O , on account of which it decomposes organic compounds, withdrawing the elements of water from them. It is saturated at about eight volumes of water, which should be the minimum addition in diluting the concentrated acid.

Sulfates are never volatile as such. They either remain involatile on ignition or else decompose, setting free SO_3 , and allowing the remaining oxides to behave according to their character. Sulfates, therefore, are to be preferred in most cases to chlorides for ignition, and the SO_4 ion should be used as the coagulant in washing solutions rather than the Cl ion, when precipitates are to be ignited.

Nitric Acid.—Reagent HNO_3 has a specific gravity of 1.42, is 69.8 per cent HNO_3 , 991 grams HNO_3 per liter, and is 15.7 normal.

HNO_3 itself is a powerful oxidizing agent in concentrated solution, decomposing to NO in presence of metals or sulfides and forming oxides or nitrates. It decomposes HCl as aqua regia, setting free Cl. In cold solution as dilute as 5 per cent it has little or no oxidizing power.

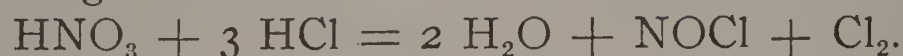
With the exception of HNO_3 , nitrates are not volatile, but decompose on heating, leaving oxides. The NO_3 ion, therefore, is a good coagulant for washing precipitates preparatory to ignition.

The solvent power of HNO_3 is low for elements such as Fe whose salts tend to hydrolysis, though all normal nitrates are easily soluble.

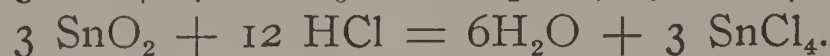
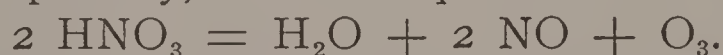
KNO_3 is the best oxidizing flux for use with Na_2CO_3 in platinum. It does not injure the crucible though it dissolves some of

it. It has the advantage over NaNO_3 that it lowers the melting point of the fusion and stays dry in the shelf bottle.

Aqua regia reacts alone as follows.



As reagent HCl is 12 normal and HNO_3 is about 16, the proper proportions for aqua regia are four parts HCl by volume to one part HNO_3 . In dissolving metals it is generally desirable to convert them to chlorides. The two acids should then be calculated separately, from the equations.



The problem is worked as follows.

Since 2 HNO_3 yield 3 of O , the equivalent of 6 of H , the normality of HNO_3 as an oxidizer is three times that as an acid, or 47.2.

Grams Sn	Cc. normal	Cc. reagent HNO_3	Cc. reagent HCl
119	4000		
	"47.2"	1	
	12		1
1	(33.6)	(0.7)	(2.6)

The minimum amount of HNO_3 , 0.7 cc. per gram, should be taken, with an allowance for incidental decomposition by HCl and for evaporation, and the necessary solution excess added to the 2.6 cc. of HCl . For small amounts of metal the incidental losses are large in proportion to the part reduced by the metal itself, but in dissolving large masses of metal the calculation is of use.

Hydrofluoric Acid.— HF is one of the most powerful solvents, particularly for SiO_2 , and must be used in gold, platinum or wax containers.

It is a gas dissolved in water, its concentration as a reagent being about 72 per cent. On boiling it loses about half its HF . As a solvent, therefore, it is more active when cold or slightly warm than when hot.

HF assists in the oxidation of metals by HNO_3 by dissolving them when oxidized, but it does not react with HNO_3 to form the equivalent of aqua regia, and the two acids can be safely used together in gold or platinum dishes. This property is particularly useful in dissolving metallic tungsten and silicon alloys, which do not dissolve in other acids.

SiF_4 , formed by dissolving SiO_2 in HF, is a gas, easily volatile. If the Si is once combined with F, its expulsion by evaporation of the acid solution to dryness is certain. If solution is complete, one evaporation and ignition is enough. Attention should therefore be directed to solution rather than to expulsion. Sand, for instance, requires long digestion rather than many expulsions.

Fluorides of metals are less volatile than chlorides. It is customary, however, to add H_2SO_4 before expelling, for safety, the bases being converted to sulfates. HNO_3 and even HCl may be used to displace HF from solution by repeated evaporation at water bath temperature.

Hydrochloric Acid and Chlorides.—HCl is a gas dissolved in water. The reagent has a specific gravity of about 1.19, 37 per cent HCl, 443 grams HCl per liter, and is 12 normal.

On boiling, HCl solutions come to equilibrium at about half the reagent strength from above and below that concentration.

HCl is one of the most powerful solvents, particularly for oxides. As it loses strength on heating it is best used slightly warm rather than hot when its full solvent power is desired.

Chlorides are generally more volatile than other salts, and should be removed from any substance preparatory to ignition. As the Cl ion is easily shown by AgNO_3 , testing filtrates for Cl serves the double purpose of showing when soluble bases are removed from the precipitate, which would give high results on ignition, and chlorides, which would give low results.

Chlorides of the alkalies, however, may be heated to temperatures below redness without loss.

NH_4Cl assists better than other ammonium salts in increasing the solubility of salts of the alkaline earths.

In quantitative analysis, chloride solutions are used perforce in H_2S separations, since HCl so often has to be used as a sol-

vent, but the precipitates are not so easily handled as those formed from HNO_3 and H_2SO_4 . Chlorsulfides instead of normal sulfides may be formed, which tend to run through the filter on treatment with alkalis. The best corrective is to keep the acidity as low as possible. The alkali should contain sulfides, which will convert the chlorsulfides to normal sulfides.

Chlorates.— KClO_3 is stable in HNO_3 solution, even when warm, but it is endothermic to KCl and the mixture is an oxidizer for sulfides, converting nascent S to SO_3 . Molar S is not acted on.



KClO_3 is a valuable aid in dissolving metals in HCl , avoiding the presence of N compounds and the danger of forming volatile H compounds such as arsene. The free Cl is easily removed by boiling.

KClO_3 acts as an oxidizer in boiling solutions on metals tending to oxidation such as Fe , when the solution is barely acid. In the case of Fe the acid set free by the hydrolysis of a neutral salt is sufficient to decompose KClO_3 .

Bromides and Bromine.—The properties of HBr are similar to those of HI , but it is slightly exothermic, and it is used in reduction only for elements which have a decided preference for the lower valence.

Bromine is a useful oxidizing agent, since it is obtained pure in liquid form. It converts S to SO_3 and Mn to MnO_2 . For the former purpose its action is increased by dissolving it in an organic liquid, such as CCl_4 , as suggested by Allen and Bishop. A. M. Smoot improved this by using acetic acid, which allows mixture with water. His mixture is Br four parts, $\text{HC}_2\text{H}_3\text{O}_2$ six parts, H_2O one part. Allen and Bishop now use a concentrated water solution of Br with KBr .³

HBrO_3 is endothermic to HBr , and is therefore a useful oxidizer of low power. In hot HCl solutions it bleaches methyl orange, by which excess is shown, and therefore it can be used in titrations. In separations it is not much used on account of the variable stability of the bromides produced.

³ Scott, "Standard Methods of Chemical Analysis."

Hydriodic Acid and Iodides.—HI is not kept as a reagent on account of its instability, but freshly formed by the acidulation of iodides it is valuable because it is endothermic and assists in the reduction of elements from a higher to a lower valence, and at the same time liberates I which can be titrated. As its reducing action is weak, the extent of the reaction is controlled by the element reacting with it, with the result that the other element is reduced to a definite valence which is stable, making titrations accurate.

Hydrosulfuric Acid and Sulfides.— H_2S is a weak acid, slightly ionized as H—HS . It forms acid sulfides with strong bases, such as KHS (or KSH), and normal sulfides with weak bases, such as PbS.

Water saturated with H_2S at room temperature is about 0.25 normal. One cc. will precipitate eight milligrams of Cu.

Coming from the generator, H_2S is likely to carry some Fe. By bubbling the gas through water this can be effectively removed.

Air and the elements which it reduces during precipitation cause H_2S to be partly converted to H_2SO_4 , so that the presence of that acid is to be counted on after an H_2S treatment.

Reactions with NH_4OH are noted under Ammonia Water.

NaSH is obtained in crystals. KSH is not. Polysulfides of both bases are obtainable, though KS_x , ordinarily called potassium sulfide, is more common.

Acetic Acid.— $\text{HC}_2\text{H}_3\text{O}_2$ is obtained as glacial acid, 99.5 per cent pure, 17.5 normal.

Another commercial strength is specific gravity 1.044, 32.5 per cent pure, 5.6 normal.

$\text{HC}_2\text{H}_3\text{O}_2$ is a very weak acid, and when its salts are added to stronger acids the acidity of the mixture is that of the $\text{HC}_2\text{H}_3\text{O}_2$ liberated.

Tartaric Acid.— $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ is a dibasic acid which is ordinarily half ionized, forming bitartrates. It is obtained in crystalline or powdered form. Its principal use in analysis is to prevent the precipitation of hydrates, as most metals form with it double salts soluble in alkalies.

While it keeps hydrates in solution, it does not interfere with the precipitation of sulfides. Elements such as Fe, which form insoluble sulfides, are easily separated by its use from elements such as Al, which do not.

With its aid Sb may be brought into solution when sulfides are decomposed or metals dissolved with HNO_3 , and it may be kept in solution without the large excess of mineral acid which would otherwise be necessary.

If tartaric acid is used in the early part of a complete analysis it is necessary to destroy it before Group 3 can be separated. This can be done in the wet way by adding HNO_3 and H_2SO_4 , evaporating to fumes of SO_3 , and completing the oxidation by further additions of HNO_3 . If much tartaric acid is present a large beaker is necessary, as a heavy froth arises.

Oxalic Acid and Oxalates.— $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ is obtained in crystals which are stable in air, and may be used as a standard against volumetric alkaline solutions and KMnO_4 .

In the presence of this acid, aided by its ammonium salt, tetravalent Sn forms a soluble sulfide. This permits the separation of Sn from the other elements of its group. In this connection it is worth noting that the oxalates of Cu, Pb and divalent Fe are but slightly soluble in water or dilute acid, and special precautions are necessary to keep them in their analytical places during the H_2S separation.

$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ is the most commonly used precipitant for Ca.

$\text{Na}_2\text{C}_2\text{O}_4$ can be obtained from the U. S. Bureau of Standards in great purity without moisture, and is the best standard for KMnO_4 solutions.

Cyanides.—KCN and NaCN are useful for keeping the three colored elements, Cu, Ni, and Co, from precipitating as sulfide in alkaline solution, permitting their separation from Cd, Bi, Zn, etc.

As these three elements are decolorized by cyanides titration methods are possible.

Care should be taken in the use of cyanides to avoid acidulating their solutions in the open room, on account of the volatile and poisonous HCN.

CHAPTER V

FUNDAMENTAL OPERATIONS

Precipitation.—A precipitate is something more than an insoluble substance. Its particles have more or less cohesion, which enables them to bridge over the pores in filters and remain while the solution passes through. They form a more or less porous mass which itself may act as a filter or in different degrees clog the filter.

The aim of the analyst is to produce precipitates which remove as much as possible of given elements or compounds from solution in forms which are easily filtered and washed. Having a solution containing an element which he wishes to precipitate, he must satisfy several conditions.

1. *Valence.*—The proper oxidizing or reducing reactions are produced, if the element is not already of a suitable valence.

2. *Precipitant.*—This is chosen with regard to the quantity necessary for complete precipitation, a slight excess being necessary in some cases and a large excess in others.

3. *Conditions of Insolubility and Cohesion.*—These include the regulation of acidity or alkalinity, heat, pressure, particularly when the precipitant is a gas, agitation, time, and the presence of electrolytes in the solution called coagulants, which cause the precipitate to cohere.

In devising a scheme for a precipitation, every one of these points must be considered, both with respect to the desired element, and also to the prevention of undesired occlusions. The theory of solutions is of value for suggestions in regard to proper conditions, but the obscure peculiarities of the different elements require experiment and observation for their accommodation. A few general rules may help.

Rules for Precipitation.—Crystalline precipitates filter best when the crystals are large. They need time in which to grow; either by slow precipitation, or by producing temporarily a condition of slight solubility, during which the larger crystals, being less soluble, grow at the expense of the smaller. This may be brought

about in some cases by boiling, in others by gradual addition of reagents, in others by agitation.

Amorphous salts, such as sulfides and hydrates, cohere best in the presence of electrolytes, such as acids and ammonium salts. Precipitates of this class which are hardest to filter are helped by giving them time to settle.

An occasional failure of a precipitation may be caused by overlooking the fact that in the ordinary course of analysis, by the neutralization of acids and alkalies, large quantities of salts are introduced, while in a shortening of the scheme the solution may be almost free from them, so that they need to be added in order to form a filterable precipitate.

Filtering.—The object of filtering being to separate a solid from substances in solution, the maximum of efficiency consists in driving the original solution through and out of the solid by means of a washing solution, with the least amount of mixing of the two liquids.

For all porous substances, such as crystalline precipitates, the most efficient form of filter is that in which the solid is collected in a layer of uniform thickness and the washing moves in a direction normal to it. The Gooch crucible and the plate filter fulfill these conditions perfectly, and they are therefore to be preferred if other conditions permit. The volume of washing solution necessary is much less than that for conical filters.

Such filters are generally used with suction, but by attaching a tube to the holder, three millimeters in diameter and about a meter long, or reaching from the table to the floor, the filtration of crystalline precipitates without suction is practicable. By the use of such tubes the filtrate may be received in a beaker, thus saving volume of washings. For some classes of work a set of ten or more such holders in a rack is a useful adjunct.

The Paper Filter.—In using a conical paper filter it is necessary to keep in mind the fact that the procedure for an empty paper is quite different from that for a large precipitate. In washing an empty filter, since draining is rapid, the washing solution tends to run over the upper part of the paper and out at the tip. Air bubbles prevent the washing from reaching the paper back of

them. Therefore the jet must be directed into the paper, either from the top, loosening the folds and allowing the solution to go between them, or else against every part of the upper half, and particularly at bubbles.

A good practice test of washing an empty paper is to saturate it with $\text{K}_2\text{Cr}_2\text{O}_7$ solution and form a routine method that is amply sufficient to wash it out.

Washing by Decantation.—A paper half-filled or more with precipitate drains more slowly, and washing the top clean is generally sufficient to insure that all the paper is well washed. But in this case the path of least resistance, instead of being through the bottom, goes around the tip of the paper, and if the precipitate tends to clog, no amount of washing will get all of the filtrate out of the tip. The proper procedure is to wash the beaker, and without waiting for the filter to drain, wash around the top of the filter. Then wash not more than twice more, enough to get the top of the paper clean. Now return the precipitate to the beaker. If it is coherent, use the rod or tube, not the wash-bottle, getting out as much as possible without breaking the paper. Now add a few drops of water at a time and mix it into the precipitate. After a soft paste has been formed so that more water can be easily stirred in without leaving lumps, wash out the filter, all but thin layers, add as much water as will fill the filter once or a little more, add such reagents as are necessary to keep the precipitate coherent and insoluble, and filter and wash as before. One decantation of this sort is enough for a sulfide or hydrate precipitate which does not fill the paper more than one-third full, and three when the paper is entirely filled.

Washing Solutions.—When precipitates tend to disintegrate and run through the filter, boiling hot water is better than cold or warm water for washing. Allowing the precipitate to stand after draining increases the tendency to run through.

Addition of the precipitant to the wash-water is sometimes enough, but it is better to add also a coagulant which does not interfere with the use of the precipitate. The ammonium salts are the best coagulants, as they need not be added in large proportions to be effective. Sodium or potassium salts must be

at least 5 per cent of the solution to be worth adding. Acids in slight proportions are effective when the precipitate is insoluble in acid. Generally the addition of the precipitant is unnecessary when the proper coagulant is used, though in some cases, particularly in filtering sulfides, the precipitant prevents decomposition by oxidation.

A paper filter will withstand a 5 per cent solution of KOH. If a somewhat stronger solution needs to be filtered, the paper should be reinforced by gauze. An acid or alkaline solution strong enough to dissolve cellulose should be filtered on asbestos.

Reprecipitation.—In some cases perfect washing is impossible, on account of the cohesiveness of the precipitate or its occlusion of impurities. Reprecipitation is the remedy. When this is necessary, the star fold is a hindrance, and the ordinary form is better. It is generally easier to control the conditions for the second than for the first precipitation, and one should therefore make sure that not only the precipitant, but also a coagulant, is present in proper proportions. The coagulant is generally formed by neutralizing the solvent with the precipitant, but if not enough of the solvent has been used, the precipitation may not be satisfactory. Therefore one should be not content with a minimum of the solvent, but should make sure that an effective coagulant will be present.

Destroying Organic Matter by Acid.—Paper and other organic matter, even coke, but not graphitic carbon, is easily oxidized and removed by the combined action of HNO_3 and H_2SO_4 . Enough H_2SO_4 should be present to cover the bottom of the beaker; the more the better, but the needs of the analysis generally limit the amount.

The more organic matter the larger the beaker, as a heavy froth may form which rises remorselessly. One gram can be destroyed in a 250 cc. beaker with 5 cc. of H_2SO_4 . To destroy an eleven centimeter filter add 10 cc. of HNO_3 and boil down rapidly to fumes of SO_3 . When the acid turns black add more HNO_3 through the lip of the beaker with a pipette or thin tube, repeating the additions until the color disappears. Pyrex beakers

will not crack under this treatment. Jena beakers used to crack occasionally. Some $(\text{NH}_4)_2\text{SO}_4$ is formed by the reaction.

During this treatment some nitrosyl sulfuric acid is formed, which is not driven out by fuming. On dilution it forms nitrous acid. This must be expelled by boiling for about five minutes before passing H_2S , otherwise a continuous decomposition of the H_2S may be started. In order to remove N compounds completely preparatory to the electrolysis of Cd, Ni, etc., the acid must be diluted slightly and evaporated to fumes two or three times.

Rapid Evaporation of Solutions.—Solutions in beakers can be evaporated more rapidly on a hot plate than on the water-bath, if left uncovered and heated just short of boiling.

Evaporation is more rapid if a piece of glass rod, bent into the shape of a fish hook, is put on the edge of the beaker under the cover on the side away from the lip, and the solution boiled rapidly. A beaker almost full boiled in this way has no tendency to bump, as it does when tightly covered.

The speed of evaporation is increased by laying an inverted cover, a size smaller, on top of the other. This makes an air space and decreases the condensation on the cover.

When solutions containing large amounts of salts are evaporated to fumes with H_2SO_4 , the critical point, when spitting is likely to occur, is when the salts are forming into a cake. A very low heat is necessary at this point. Adding the H_2SO_4 at a concentration not quite enough to form the cake and evaporating on the water-bath until the cake is formed, finishing on the hot plate, saves attention.

METHODS OF DECOMPOSITION

Alloys.—Most alloys respond best to a preliminary acid treatment, the choice of acids depending on the major constituents.

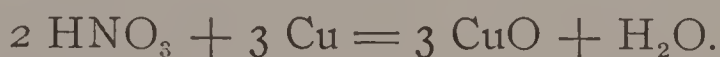
HCl.—All metals except silver form soluble chlorides, but those electro-negative to hydrogen do not dissolve in HCl without an oxidizer. It is often advantageous, as in the case of alloys high in Pb, to boil the finely divided sample with concentrated HCl until it is entirely decomposed, leaving a residue of Sb, Cu, etc. The beaker is then removed from the heat, and KClO_3 stirred

in a little at a time until there is free Cl in excess, which is then boiled out, leaving a clear solution. While PbCl_2 has a low solubility in cold HCl solutions, it is easily soluble when hot, and Pb dissolves as readily as its position in the electro-potential series indicates, if enough solution is provided to keep the PbCl_2 from covering the undecomposed alloy.

Since PbCl_2 crystallizes from acid solution in great purity, it is often convenient to separate the bulk of the Pb in this way before proceeding with the analysis.

Lead Chloride Separation.—Boiling HCl reaches constant composition at about 50 per cent of its reagent strength, whether weaker or stronger before. At about 20 per cent the solution holds the least Pb per unit of HCl. Therefore to separate PbCl_2 it is best to concentrate the HCl solution to 20 or 30 cc., or until PbCl_2 begins to separate, add double its volume of water, and allow it to cool, best over night. The PbCl_2 is then filtered out and washed with cold 5 per cent HCl. No more PbCl_2 will separate in the filtrate unless it is further concentrated.

Aqua Regia.—Aqua regia is theoretically composed of three parts HCl and one part HNO_3 , but in practice it is better to calculate the amount of HNO_3 necessary to oxidize the sample by its decomposition to NO, adding a slight excess over that, enough HCl to give the desired excess, and enough water to keep the action from being too violent. The typical reaction is as follows.



Combining this with HCl we have,



Aqua regia is particularly useful for alloys high in Sn, which do not dissolve in HNO_3 , and in which there is danger of losing some As as AsH_3 and possibly Sb as SbH_3 when dissolved in HCl alone. Also the solution is completely oxidized and free from alkali salts. When such an alloy is treated with aqua regia, the Sn dissolves first to a colorless solution, the electro-negative elements precipitating upon it. The solution is quiet until all Sn is dissolved, and then the precipitate dissolves, sometimes with explosive violence. It is necessary to use a large beaker and to have a pan of water ready to check the reaction.

Alloy Mixture.—A good mixture to dissolve any SnPb alloy is composed of H_2O 40 cc., HCl 30 cc., and HNO_3 4 to 5 cc. This will dissolve a gram of Pb by simmering or gently boiling for half to three-quarters of an hour.

A good mixture for ten grams of tin alloy is 25 cc. water, 50 cc. HCl and 15 cc. HNO_3 , in an 800 cc. beaker.

HNO_3 .—All alloys low in tin and antimony may be dissolved in HNO_3 , the Sn remaining almost undissolved as metastannic acid. Sb forms an equivalent compound, and if there is four times as much Sn as Sb, the Sb will also be completely precipitated, though when alone its solubility is considerable. As in small proportions is also held by metastannic acid, and also part of the Fe, Mn and Cu. Most other elements are completely soluble under these conditions, except that PbSO_4 may be formed by the oxidation of S in the sample. This can be prevented by using an equal amount of water with the HNO_3 . There are many schemes for the complete separation of Sn from other elements by HNO_3 , but in the writer's experience none of them are successful, the precipitation of Sn is never complete, the precipitate is never pure, and the complete separation of Pb by diluting the HNO_3 is more important than any other consideration.

High Oxidation Mixtures.— HNO_3 with a little HCl is useful for oxidizing S in some alloys. A saturated solution of KClO_3 in HNO_3 is more efficient. The concentration may be increased by dissolving the salt to saturation on the water-bath, as the two compounds do not decompose each other even when heated. The solution should be cooled before use, and the reaction with the sample should be retarded by moving the beaker about in a pan of water. The full amount of the mixture should be added at once, as when the KClO_3 is not in excess the reaction proceeds with HNO_3 alone, as is shown by the presence of red fumes, and the oxidation of S may not be complete.

Bromine alone is not useful on account of its volatility. In combination with HNO_3 or HNO_3 plus a little HCl , it helps the oxidation some. Its best use, however, is in solution with an acid, in which form it is less volatile and makes a better con-

tact with the sample than when used alone. A. M. Smoot uses a mixture of two parts bromine and three parts acetic acid. This mixture will convert crystals of sulfur to sulfuric acid. The sample should be allowed to stand cold in contact with the mixture for several hours, and then treated with some other acid.

H₂SO₄.—Dilute sulfuric acid dissolves only those metals which are electro-positive to H. Lead, though in this class, is kept from dissolving by a coating of PbSO₄ which forms quickly. On account of its high normal value and the low solubility of many of its compounds it is best used in dilute solutions, about one part in ten.

Hot concentrated H₂SO₄ is a powerful oxidizer, all but the noble metals decomposing it and forming sulfates. It is particularly useful for the treatment of alloys for volumetric work, in which nitrates must be avoided. Its action is helped by the addition of K₂S₂O₇, which raises its boiling point and allows a higher temperature in an open vessel. The products of this reaction, if not soluble on dilution, will dissolve easily on the addition of HCl.

Solution in Alkalies.—Aluminum alloys are conveniently dissolved in NaOH or KOH. This is not only a better solvent than any acid, but it has the advantage of concentrating most of the other elements in the insoluble residue. The danger of frothing should be guarded against.

ORES, ACID TREATMENT

Sulfides.—Some sulfides are decomposed by HCl, but in most cases where its use is theoretically possible, as for instance in the treatment of stibnite, there is generally some good reason for not using it. In the case of stibnite, weathering often forms oxides insoluble in HCl, and the residue requires a separate treatment. As it is just as easy and somewhat safer to fuse the whole sample, the use of HCl is not advisable except for samples of known purity.

Nitric acid decomposes all sulfides with liberation of sulfur. As tin seldom occurs as sulfide it is not likely to be found in the nitric acid solution of an ore, though tin from stannite will

dissolve. The addition of tartaric acid permits the solution of stibnite in HNO_3 , though the objection to its use is the same as for HCl .

Sulfuric acid is seldom used to decompose sulfides directly, though it is useful in combination with HNO_3 , the latter being driven off by evaporation after the ore is decomposed, converting the soluble portion to sulfate. When a mixture of HNO_3 and H_2SO_4 is used, it is generally best to add an equal volume of water, which gives a better solvent effect.

Oxides.— HCl is by far the best solvent for oxide ores containing much iron. When an ore is to be completely decomposed for analysis, the start is generally made with HCl .

HNO_3 is used as the solvent for the assay of ores of Cu , Zn and other elements whose oxides are easily soluble in it. It is convenient, because the same mixture can be used for all ores of these elements, whether oxide or sulfide.

Sulfuric acid is used to drive off HNO_3 as for sulfides, but seldom for direct decomposition.

Mixed Ores.—Hydrofluoric acid is often useful for liberating some element from combination with or occlusion by SiO_2 . It is not always necessary to dissolve all of the silica, as the desired element may be in fissures in the quartz, and the acid, by dissolving the silicates, will search out the pores, leaving pure quartz. HF treatment is conveniently done in a platinum or gold dish, H_2SO_4 being used to drive off the more volatile acid after it has done its work.

When it is necessary to dissolve ferric oxide and also to decompose sulfides, it is better to use HCl first, following with HNO_3 . The solvent action of HCl on oxides is much greater alone than in combination with HNO_3 , while the oxidizing action of HNO_3 is helped by the presence of HCl . The solvent power of HCl is greater when it is slightly warmed, but not heated enough to weaken it by evaporation.

Slags and Soluble Silicates.—Slags are often so high in silicates that if acid is poured on a sample and allowed to stand a cake is formed which hinders decomposition. This trouble is prevented by dissolving the silicic acid as it forms.

To a gram of slag add 25 cc. of boiling water and then, while shaking, 10 cc. of HCl, a little at a time, keeping the sample in motion until it is nearly or quite dissolved. By adding more water and adding the acid while the water is boiling less manipulation is required. After the action of the HCl has ceased, add 5 cc. of HNO_3 to dissolve sulfides and oxidize iron, boil until SiO_2 begins to separate, and evaporate to dryness on the water-bath.

If it is desired to separate the H_2S group only, use 100 cc. of water per gram of sample, HCl in slight excess, no HNO_3 , boil only until the solution of silicates is complete, pass H_2S and filter hot. The more soluble slags are easily handled in this way without separating the SiO_2 .

Insoluble Residues.—After the acid treatment it is often necessary to separate the residue and treat it differently, generally by fusion, though sometimes by HF as above.

The residues insoluble in acids are generally themselves of acid nature, and require alkaline treatment. This is more easily given by fusion than in the wet way, not only because a stronger action is so obtained, but because alkaline solutions attack most containing vessels.

Filtration of the Insoluble Residue.—The residue may consist in part of gelatinous silica from the decomposition of silicates. For this reason all ores are thoroughly dehydrated before filtering. If H_2SO_4 has been used, the acid is heated enough to give white fumes of SO_3 , showing that not only the HNO_3 but also the water has been expelled, making the silica insoluble.

In other cases, the sample is evaporated to dryness and baked at a temperature somewhat above 100° to make sure of dehydrating the silica. This baking is more safely conducted on a plate heated by gas than is the case after fusion, as there are no alkali salts present which might form soluble silicates. Account must be taken here of the volatility of FeCl_3 under these conditions. If Fe is to be determined, the heat should be under thermometer control in an oven.

After drying, in most cases HCl is used to take up the soluble portion. After warming the concentrated acid, water is added.

The filter must be arranged with care, for the residue is not a precipitate, unless it consists partly of decomposed silicates, and may not cling to the filter. The paper should be folded in the ordinary way, without tearing off the corner, and some pulp should be poured in around the top, to close the channel at the back and keep the column, as well as to reinforce the paper. In most cases water is used for washing, but acid may be necessary, as in the treatment of zinc retort cinder, to keep the residue from running through. As a general thing, HCl should not be used to wash a residue for ignition, as so many chlorides are volatile. HNO_3 is better, or H_2SO_4 may be used.

Some residues, such as those of waste products containing Sb, will suffer loss by reduction to volatile forms on ignition of the paper. They may, if the elements of asbestos are not the subject of the assay, be filtered on a Gooch crucible, the mat dried, removed and fused with the residue. For this purpose a holder that transmits the filtrate safely is necessary.

Choice between Fusion of the Entire Sample and Fusing the Insoluble Residue.—When the residue can be ignited without loss it is generally preferable to treat the sample with acid first and fuse the residue with Na_2CO_3 in platinum.

It is hardly ever worth while to fuse with $\text{K}_2\text{S}_2\text{O}_7$ a residue insoluble in acid. Such a residue needs an alkaline flux.

The combination method permits the use of a larger sample than the fusion alone will accommodate, protects the major part of it from the vicissitudes of the fusion, and allows the use of platinum with more safety. The principal objection is that it takes no more time to fuse the sample from the start than to fuse the residue alone, so that time can be saved by fusion, particularly when Na_2O_2 is used as the flux.

The Bisulfate Fusion.— $\text{K}_2\text{S}_2\text{O}_7$, ordinarily called bisulfate, may be fused in platinum, silica or porcelain. It has a slight solvent action on platinum, but none on silica or porcelain. Porcelain is particularly adapted to this flux, as the smooth sides of the crucible permit the melt to be dropped out after cooling. The crucible must be protected against drafts while hot, but aside from that its tendency to crack is less than that of silica.

The pyrosulfate should be thoroughly dehydrated. Old material should be remelted before use. It may be added in large pieces, though quicker and more complete action is obtained by mixing the residue with the powder. The heat should be gradually increased, so that the excess acid may not be driven off too soon. The rule is to apply just enough heat to keep it melted, raising the heat from time to time when it begins to harden, until the full heat of a Bunsen burner is necessary for fusion, the finish being at a bright red heat. An outer crucible should be used at first, and removed when high heat is required. This flux does not automatically wash down the sides of the crucible. If any of the residue is above the surface, the crucible should be manipulated to cover it with the flux and bring it under. A dark-colored residue is easily seen through a porcelain or silica crucible if a white light is held below, so it is possible to tell how the fusion is proceeding. It should occupy a full hour. When the lid is removed for examination, it should not be inverted, as the spatter or distillate is very liquid.

The melt should be allowed to cool quietly. When cold, hold the crucible over a beaker and clap it sharply against its lid. This will loosen the bulk of the precipitate. Let it fall into the beaker. The crucible should then be filled with hot water, covered with its lid and allowed to stand a few minutes, when it can be washed out into the beaker. A little extra acid helps the leaching.

The bisulfate fusion is essentially an acid treatment, and is suitable only for oxidized material, either ignited precipitates, oxide ores or residues which have been treated with HF.

Sodium Carbonate Fusion.—A platinum crucible is generally used for this fusion, though nickel can be used. It is important to avoid substances which will injure the crucible. Lead in most cases can be removed by HCl, unless there is a combination of Pb and Sb. The addition of a little KNO_3 will generally protect the crucible against alloying, by keeping the metals oxidized. It is during the ignition of the paper that most of the alloying occurs, and this may be done in porcelain in case of doubt, and the residue after thorough oxidation transferred to the platinum for fusion. Even litharge can be fused in this way in platinum without alloying, though an adherent coating may form.

The result of the sodium carbonate fusion is to convert all silica and other acid radicals into sodium compounds soluble in water. Alumina is slowly converted to sodium aluminate, requiring in some cases long heating at blast temperature. It is the best flux for fused alumina, which is practically insoluble in acids.

Before cooling the melt, it should be put into better form for solution than when left in the bottom of the crucible. It may be poured into a platinum dish floating in water. If the melt is not too large, it can be poured into the lid of the crucible, supported level on a porcelain crucible. For this purpose there should be no crack in the lid, or the melt will find it and run through.

The writer prefers to rotate the crucible while cooling, since this leaves the melt in a thinner layer than when poured. As it is best to dissolve the melt entirely before acidulating, no time is lost, though it may take longer to get the crucible clean.

After the melt has hardened, the crucible is put into a platinum dish or porcelain casserole and leached out with the least amount of hot water. It is easier to get the crucible clean if it is entirely leached and polished before acidulating. Then the oxides are dissolved by filling the crucible with acid, pouring this into the carbonate solution.

Niter and Soda Fusion.—The technique of this fusion is the same as that of the sodium carbonate fusion, except that it must be leached in porcelain, or else acidulated with HNO_3 to avoid dissolving the platinum dish. The same precaution applies to the ordinary carbonate fusion if any KNO_3 has been added. The use of this fusion is principally to convert sulfides to sulfates. The KNO_3 should not be more than $1/20$ of the Na_2CO_3 , and preferably barely enough to perform the necessary oxidation.

Fusion Mixture.—Sodium and potassium carbonates mixed have a much lower melting point than either alone. The lowest melting point is made by mixing them in molecular proportions, though most of the advantage is gained by the addition of a very little of one to the other. By using this mixture a fusion can be made in porcelain with little difficulty, and easily in nickel.

Sodium Peroxide Fusion.—This fusion can be made in porcelain, nickel or iron, each having some advantages.

In porcelain, no metal is introduced into the melt, which makes it useful for oxidizing such elements as chromium preparatory to titration. As the flux dissolves the crucible rapidly, the operation must be so conducted as to decompose the sample without loss of time. It should be finely ground and well mixed with the flux. A cover of unmixed flux helps to prevent loss. The crucible should be heated almost to fusion over a Bunsen burner. It may then be taken in tongs and manipulated in a large mild blast flame, to bring the heat up quickly and evenly. As soon as the flux is enough melted to flow it is rotated so as to bring in all of it and then heated quickly almost to the temperature at which it spatters. Another method is to support the crucible covered on a triangle, removing the lid momentarily to watch it closely until the flux is melted in the middle, then remove the flame and then the lid, finishing by manipulation over the Bunsen flame. The melt is allowed to harden in mass.

In nickel or iron, since a larger crucible is used, no cover is necessary, and preliminary heating is not necessary, though it saves time, one crucible being heated over the Bunsen flame while the next is manipulated over the blast. An iron or nickel crucible can be used safely until the bottom is flexible in the hand.

These crucibles melt through the bottom more easily if the sample has not been well mixed with the flux or if a sharp blast is used, in either case raising one point to the ignition temperature of iron.

For leaching, the crucible should be laid on its side in a sufficiently large beaker, held in place by standing a rod in it. Cold or warm water is poured in just enough to dissolve the melt, allowing it to mix itself.

The crucible should then be stirred in the solution before policing, which makes it easier to clean. After policing, it is good practice to wipe it dry immediately, so that it will not rust.

If it is not necessary to keep the volume down, the crucible may be covered with hot water, which is better if the insoluble part is to be filtered in the alkaline solution. Before filtering, the solution should be diluted to 5 per cent to avoid breaking the paper, if an ordinary filter is used.

The scales of iron or nickel from the crucible are easily soluble in a sufficient excess of HCl , which should be added in bulk to avoid precipitation of silica. Oxalic or sulfuric acid will dissolve the scales, though not so readily as hydrochloric acid.

Sulfur and Soda Fusion.—It is customary to make this fusion with equal parts of sulfur and sodium carbonate. A better mixture is Na_2CO_3 100 parts, K_2CO_3 140 parts, and S 100 parts. This gives a lower melting point, and the sulfur is sufficient, as it is twice as much as is necessary to combine with the bases, the excess volatilizing quickly in any case.

Pure amorphous oxides of tin and antimony are so easily fused in this flux that it is not necessary to mix them before heating, only enough heat to give complete fusion being necessary. It is an interesting experiment to use a glass cover for this fusion, through which its phases can be seen without admitting air. The cover should be no wider than the crucible, or the flame will crack it.

Such minerals as cassiterite require long fusion at the highest temperature of the Bunsen burner, using a chimney. Even then it is often necessary to filter the solution and fuse the residue.

The melt is best leached in cold water, as this allows the sulfides to settle and filter better than when heated. Stirring while leaching should be avoided. The flux is entirely converted to alkaline polysulfides.

If the solution after leaching shows a green color from colloidal Fe, it can be cleared by adding an ammonium salt in excess over the Na. As the capacity of NH_4 for S is less than that of Na, it will be necessary to add also some NH_4 to prevent the precipitation of S.

If NH_4 salts are not wanted, add Na salts, at least 10 per cent of the solution. NH_4 salts are more efficient in precipitating Fe, but increase the solubility of Cu.

Sodium Hydroxid Fusion.—This fusion is made in silver. In order to avoid loss by spattering, it is best to melt the flux in the crucible to drive out water, cool it, put the sample on top of the cake, and melt again. This fusion is good for removing gangue from graphite.

CHAPTER VI

QUALITATIVE ANALYSIS

PREFACE

The scheme of qualitative analysis here given is not intended to give methods of identifying the elements with the least amount of work. It is intended to show how the different elements can be separated quantitatively from each other, and to give practice in recognizing and handling them in the forms in which they usually appear in course of quantitative analysis.

Quantitative analysis is a profession, or rather a trade. Qualitative analysis is an occasional expedient. It is generally performed by one whose occupation is quantitative analysis, and who will naturally use the methods with which his daily work keeps him familiar.

By following as closely as possible ordinary quantitative procedure in qualitative analysis, the student will gain the practical knowledge which he will be able to use in any analytical work; he will be able to turn any qualitative test into a quantitative test; he will avoid cumbering his mind with information of little use.

QUALITATIVE ANALYSIS

GENERAL SCHEME

Reagents.—When quantities of reagents are mentioned, they are understood to be in the form in which chemical houses supply them; either in concentrated solution or dry. Acetic acid is supposed to be glacial, and if only a weaker solution is available account must be taken of the water in it.

Condition of the Sample.—If the sample is an alloy, it should be in particles as small as the sawings of a hacksaw. If it is a soluble salt it need not be fine, but otherwise non-metallic samples should be fine enough to pass an 80-mesh screen; that is, 80 wires to the inch.

GROUP 1.

Classification of Samples

Method A:*Case 1.*

1. **The Sample is a Liquid.**—A liquid sample must first be examined to find out what proportion of solid matter it contains. Measure 10 cc. of it into a porcelain dish and evaporate it to dryness on a plate over a Bunsen Burner. Scrape out the residue and weigh it. Calculate the volume of the original solution that must be taken to contain one gram of solids.

2. Measure the volume that will contain one gram of solids into a 150 cc. beaker and dilute it to 100 cc. with hot water. In any case take no more than 100 cc. If a precipitate forms when water is added, the sample cannot be treated by Method A. Measure out a fresh portion without diluting it and treat it by Method B.

Note. In this and all other cases where the volume of the solution containing the sample is to be measured, the measurement is by comparison with water measured into a beaker of the same size.

If no precipitate forms on dilution, the next step is to find out whether the sample is neutral, acid, or alkaline. Drop in a

piece of litmus paper not larger than one square centimeter. Red is acid, blue is alkaline, and purple is neutral. On account of its clear indication of neutrality litmus paper is preferred for these tests.

3. If the Sample is Neutral.—Add 2 cc. of HNO_3 , heat the solution to boiling, add a drop of HCl , and stir well. If no precipitate forms the sample contains no Ag nor Hg' . Mark the beaker Group 2, and proceed as directed under that head.

If a precipitate forms, add another drop of HCl , and look closely to see if fresh precipitation follows it. If it does, stir, allow it to settle, and test again. Continue until no more precipitate is formed. Avoid adding too much HCl , as AgCl is soluble in strong acid.

Prepare a filter large enough to hold the precipitate without filling it more than half full, or at least a nine centimeter paper, and pour in a little paper pulp to make sure that the precipitate does not run through. Filter into a 150 cc. beaker. Remove the filtrate and mark it Group 2, and proceed with it under that heading when convenient.

Put a fresh beaker under the funnel and wash out the precipitation beaker and then wash the filter thoroughly with hot water. Receive a few drops of each washing in a clean cover-glass which contains a drop of 5 to 10 per cent AgNO_3 solution. At first a precipitate of AgCl will form from the excess HCl washed out of the paper. When the precipitate no longer forms in the washings, the HCl , and presumably the other constituents of the filtrate, have been washed out of the filter.

Note. If the previous precipitation and washing have been performed without allowing the solution to cool, any Pb that may be in the sample will remain in solution, and will be found in Group 2. Otherwise some of it may be found in the hot water washings.

4. The precipitate insoluble in hot water may be either AgCl or HgCl . Remove the washings and put a clean beaker under the filter. Pour NH_4OH into the filter and see if any of the precipitate dissolves. Stir the mixture in the filter with a rod, being careful not to break the paper. AgCl will dissolve in

NH_4OH . HgCl will not dissolve, but will turn black, from reduction to metallic Hg. Both may be present. To confirm the presence of Ag, dilute the NH_4OH filtrate to double the volume, put in a piece of litmus paper, and add HNO_3 slowly with stirring until the solution is acid. If Ag is present, AgCl will precipitate.

AgCl will turn first purple and then black on exposure to daylight.

5. If the Liquid is Acid.—It is necessary to find out how much acid it contains. Add NH_4OH a few drops at a time, with stirring, until the solution is exactly neutral to litmus, and then add 2 cc. of HNO_3 in excess. If a precipitate forms which does not dissolve in this excess, add 2 cc. more. If then it does not dissolve on stirring, take a fresh sample and use Method B, as Method A is suitable only for low acidity.

If the sample proves to be suitable for Method A, heat the solution to boiling and make the HCl precipitation and separation as directed for the neutral solution, (3), reserving the filtrate for Group 2.

6. If the Liquid is Alkaline.—Add HNO_3 a little at a time with stirring until the solution is neutral, and then 2 cc. more. If a precipitate forms when the solution becomes neutral or acid, it may or may not be AgCl , but not HgCl , as Hg' would not be present in an alkaline solution. If the precipitate appears different, either in color or form, from a freshly prepared AgCl precipitate, it will not be convenient to use Method A. A fresh portion should be measured out, neutralized with HCl , and treated by Method B.

If no precipitate appears when the solution is made acid, or if it appears to be AgCl , heat the solution to boiling and add HCl as directed for the neutral sample, (3), continue the separation and reserve the filtrate for Group 2.

Case 2:

7. The Sample is Solid, but Soluble in Water.—Weigh one gram into a 150 cc. beaker and add 100 cc. of hot water.

If the Solution is Acid or Neutral.—Add 2 cc. of HNO_3 and proceed as directed for the neutral sample, (3). Many salts will

dissolve but by hydrolysis form a slight precipitate. If such a precipitate remains after adding 2 cc. of HNO_3 , add 2 cc. more and stir well. If the solution clears, proceed by (3). If it does not, treat a fresh portion by Method B.

If the Solid Dissolves to an Alkaline Solution.—Treat the solution by (6), using Method B if necessary.

Case 3:

8. The Sample is Solid and Insoluble in Water.—Grind the sample fine and weigh three portions of 0.5 gram each into 150 cc. beakers, three different tests being carried on as much as possible together, until it is decided which of them is most convenient.

Method B:

9. For Alloys and Salts, but not for Ores.—Alloy mixture. Mix 200 cc. of H_2O , 150 cc. of HCl , and 20 cc. of HNO_3 .

The use of this mixture cannot be reduced to a rule, as some substances will not dissolve in it, but it is well suited to some others, particularly lead alloys, which are hard to dissolve completely.

Try adding 25 cc. of the mixture to one portion of the sample and boil slowly for about fifteen minutes. If it dissolves partly, continue the boiling, adding more mixture from time to time to keep the volume to 25 cc. If the sample does not dissolve completely in an hour, do not use the method. If the solution is complete, raise the cover slightly by hanging a glass hook on the side of the beaker away from the lip and boil the solution down to about 10 cc., or a little more if crystals cause bumping. Add 10 cc. more of HCl and continue the boiling to 10 cc. again. Add a second 10 cc. of HCl and boil down again. This is to remove HNO_3 . Add double the volume of hot water, stir well and set it away to cool, preferably over night.

If much Pb is present, a curdy precipitate of PbCl_2 will form during the boiling, or on adding the water. PbCl_2 may also crystallize from the cooling solution as brilliant needle-like crystals. The chemist can identify Pb with certainty by the appearance of these crystals, after he has become familiar with them.

Ag, if present in quantity, will form AgCl , but a few milligrams will remain in solution. Hg will be divalent, and will not precipitate.

After cooling, filter the solution on a small filter and wash it once with 5 per cent HCl . In order to insure the complete precipitation of the remaining Pb in Group 2, it is necessary to reduce the acidity to 2 per cent. Neutralize the filtrate with NH_4OH , add 2 cc. of HCl in excess, and dilute to 100 cc. If a precipitate forms which does not dissolve in the required excess, measure in enough HCl to dissolve it, and keep a record of the amount. After passing H_2S to precipitate the bulk of the elements which had hydrolysed, enough water can be added to dilute the excess HCl to 2 per cent and the H_2S treatment continued.

10. Returning to the PbCl_2 precipitate, put a fresh beaker under the filter and wash it four times more with 5 per cent HCl . "One washing" is a conventional term whose meaning varies with the practice of different chemists. In these notes it indicates the amount which is sufficient to remove almost all of a colored solution from an empty filter. This will take about 10 cc. of solution, applied in a jet on the upper edge of the paper, directed down into the folds of the paper, mostly on the triple side.

Discard the washings, put a clean beaker under the filter, and pour hot water on the precipitate. PbCl_2 will dissolve, leaving AgCl . Continue washing with hot water until no more of the precipitate dissolves. Mark the solution Pb and reserve it. Test the residue on the paper for Ag as in (4).

Ammonium Acetate Solution.—Pour into a beaker successively 8 cc. of NH_4OH , 10 cc. of water, and 7 cc. of glacial $\text{HC}_2\text{H}_3\text{O}_2$. If the acid is weaker than glacial, leave out the water and pour the acid into the NH_4OH until the mixture is acid to litmus.

11. Add 25 cc. of the $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ solution to the Pb filtrate, stir to dissolve any crystals, and add solution of $\text{K}_2\text{Cr}_2\text{O}_7$. A yellow precipitate confirms the presence of Pb.

Method C:

12. For Alloys Free from Sn and Sb, and for Sulfide Ores.—Add 5 cc. of water and 5 cc. of HNO_3 . Warm on the water-bath or on a hot plate at a temperature below boiling for half an hour, or until no more red fumes remain in the beaker. Then add 20 cc. of water and heat to boiling. Metallic Pb will dissolve better in the more dilute acid, so if the sample seems to consist mostly of Pb, the acid should be diluted at the start. Keep the solution at boiling heat for half an hour if there seems to be action, adding more water when necessary to keep the volume of the solution. If the sample does not dissolve completely, or if there is a milky residue, it is evident that the method is not suitable. Free S may be disregarded, except to record it as evidence of the presence of sulfides.

If a sandy residue remains from an ore, examine it carefully. If it appears to be ordinary sand, it may be so recorded and discarded. If it contains colored minerals it may be fused with Na_2O_2 as in (15).

If the method is satisfactory, filter into a 150 cc. beaker. Dilute the solution to 100 cc. with hot water and test for Ag as in (3). Hg' will not be present, owing to the oxidizing power of HNO_3 . The solution remaining from the Ag test is reserved for Group 2.

Method D:

13. For Ores, Particularly those Containing Oxides.—To the half-gram sample add 25 cc. of HCl and let it stand on the water-bath or a hot plate at a temperature below boiling for half an hour.

Note: Ten cc. of HCl is enough except as a test for W.

It is good practice to let it stand cold over night before heating, as HCl rapidly loses strength on heating. Then add 5 cc. of HNO_3 , boil down to about 5 cc., remove the cover and evaporate to dryness without further boiling. Add 10 cc. of water and 5 cc. of HCl, cover and warm until the soluble portion has dissolved. Add 25 cc. more of water, stir and allow it to cool.

14. Filter and wash five times with 5 per cent HCl. Reserve the filtrate for Group 2. Put a fresh beaker under the funnel and wash with boiling water to test for Pb as in (11). Treat

the residue with NH_4OH as in (4) and test for Ag. Use only a small part of the NH_4OH filtrate for the Ag test. If the sample contains W, part of it will be dissolved in HCl and reprecipitated as yellow WO_3 , insoluble in acid but readily soluble in NH_4OH to a colorless solution. If the presence of W is suspected, part of the NH_4OH filtrate should be evaporated to dryness in a porcelain dish and ignited. WO_3 will appear, red when hot and yellow when cold, with perhaps a tinge of green from reduction. Ag is not likely to be found in the same sample with W, but Sn is, and the latter will remain on the filter, insoluble in either acid or NH_4OH .

15. Sodium Peroxide Fusion of the Insoluble Residue.—Wash the residue from the paper into the beaker and examine it carefully. Any of a great variety of minerals may be present, which are insoluble in acids.

Quartz grains, sand, are most common; transparent and colorless or slightly tinted. Common rock materials, consisting of silicates of Ca, Mg, Al, Fe, etc., come next. They are often of a greenish color but may be white or black. Many of them form flakes or scales, like mica.

Barytes is normally white and amorphous, but may be discolored. Undecomposed WO_3 is brown. Cassiterite is generally colored brown by Fe_2O_3 . Oxides of other elements such as Sb may be white or colored.

All of these are fusible in alkalies, and all of the materials are made soluble except Ba, which changes to insoluble BaCO_3 on leaching a carbonate fusion in water, but which reverts to insoluble BaSO_4 if the solution is acidulated while the SO_3 from which the fusion separated it is still present. SiO_2 in small quantities will be completely dissolved and will remain in solution in both the alkaline and acid solutions, until the latter has been concentrated by evaporation.

Record the appearance of the residue for comparison with its analysis. Return it to the filter, put it in a nickel crucible and burn off the paper. Add from two to five grams of Na_2O_2 , according to the size of the residue, using five if the sample is almost all insoluble. Fuse over a Meker burner, holding the

crucible in tongs and rotating it obliquely to hasten the fusion. Allow the crucible to cool, put it into a 250 cc. beaker, add 100 cc. of water, leach out the crucible and remove it. Add 2 cc. of 1:1 H_2SO_4 and just enough HCl to dissolve the precipitate of hydrates. Allow the solution to settle and decant into another beaker, marking it Group 2R. Examine the residue. There will be some black scales from the crucible, which should be disregarded. If the sample contains Ba, it will be found in this residue as white amorphous BaSO_4 . Sr may also be present, with the same appearance. If this white residue is found, dissolve the crucible scales away from it with 20 per cent HCl , dilute, filter, ignite, fuse with Na_2CO_3 in platinum or nickel, leach with water, filter, dissolve the residue in a little HCl and test the solution in the flame for Ba and Sr.

GROUP 2

17. The object of the preceding operations is to get the sample into condition for the H_2S precipitation. Incidentally some elements, SiO_2 , Ag, Hg' , Pb, W, Ba and Sr may have been identified, though traces of any of them except W and Ba may remain undiscovered in solution.

The elements which may be found in Group 2 are As, Sb, Sn, Se, Te, Mo, Ag, Hg, Pb, Cu, Bi and Cd. Note that the first six form sulfides soluble in alkalies, while the sulfides of the second six are insoluble. As, Sb, and Sn are common and Se, Te, and Mo are rare. Pb and Cu are often found in quantity, while Ag, Hg, Bi and Cd are either rare or generally found in traces.

In Chapter III will be found the acid conditions for the H_2S precipitation of most of the elements. Pb requires the lowest acidity; not more than 2 per cent HCl for certainty of complete precipitation. Other elements, such as Sb, if present in large quantity, may require a higher acidity than that to keep them in solution before precipitation.

Not more than 5 per cent of free HNO_3 should be present, and H_2S must not be passed through a hot HNO_3 solution. If both nitric and hydrochloric ions are present, as is the case when either acid is mixed with salts of the other, there is danger that

the H_2S will be decomposed and the precipitation fail. This danger is increased by heat and high acidity. Therefore it should be avoided when possible, and when necessary the solution should be kept cold and the acidity should be kept as low as will keep the elements in solution before passing the gas, preferably from 1 per cent to 2 per cent.

HCl may be present in any proportion without affecting H_2S , but the greater its concentration the fewer elements will precipitate. The best strength is just enough to keep all the elements in solution. This need never be more than 5 per cent, and preferably should be from 1 per cent to 2 per cent.

H_2SO_4 may be used mixed with either HCl or HNO_3 without affecting the H_2S precipitation, but the total acidity will be greatly increased if it is added to a solution containing nitrates or chlorides, owing to its high normal ratio.

Oxidizing agents such as H_2O_2 or reducing agents such as H_2SO_3 must not be present during the H_2S precipitation, as they will decompose H_2S .

18. There may be two solutions for the H_2S precipitation, 2 and 2R, which must be kept separate because 2R contains some of the crucible, and 2 has to be tested for that element. Regulate the acidity of 2 if necessary for complete Pb precipitation, and pass H_2S into both until precipitation appears to be complete. If 2 is too strong for Pb on account of other elements, pass the gas until the other elements are precipitated and then add enough water to dilute the acidity (HCl) to 2 per cent and pass the gas again. The collecting and easy settling of the precipitate is an indication of complete precipitation. If in doubt, filter a little of the solution and pass the gas into the filtrate.

19. Prepare a filter amply large for each precipitate, so that it may spread in a thin layer and not form a lump. A little pulp will help to keep the precipitate from running through. Filter and wash the precipitates once, remove the filtrates, mark them 3 and 3R, and boil them. In the meantime wash the precipitates thoroughly, by decantation if they are large enough to form a level surface across the filter, with water containing 1 per cent HCl and some H_2S . Test the washings by letting them

run into an excess of NH_4OH until they no longer show the presence of the lower groups by darkening the solution. Wash the beaker at first and the precipitate at last, with water, to remove most of the acid.

20. Removing As and Mo.—In the meantime watch the boiling filtrates 3 and 3R to see if any precipitate forms.

If pentavalent As is present in quantity it will not all be precipitated at first, and some will separate by reduction on boiling the filtrate. If it appears, distinguished by its being yellow while the finely divided S which always separates is white, pass more H_2S , filter on a separate filter, and boil the solution again. If more As separates, the operation will have to be repeated until it is all removed. The H_2S should be passed for at least fifteen minutes each time.

Mo also is likely to be incompletely precipitated, and the filtrate may be colored deep blue by it, perhaps modified to green by other elements, and a brown precipitate may form on boiling. The incomplete precipitation is due to reduction, and the Mo has to be reoxidized before it can be completely precipitated. This is done by oxidizing the Fe as in (21). Before passing H_2S again the acidity must be reduced to 1 per cent and the solution cooled. It may be necessary to repeat the oxidation of the filtrate to remove a large quantity of Mo.

Often, when Mo is present, it is the only element to be tested for. The regular assay method is then preferable.^{3*}

Test for H_2S .—Hold a piece of paper moistened with solution of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ in the steam from the beaker. If H_2S is present the paper will be darkened.

21. Oxidation of Fe.—All H_2S should first be boiled out. Allow the solution to cool slightly, add a slight excess of KClO_3 over the most Fe that might be in the sample, and boil for a few minutes. KClO_3 will oxidize more than double its weight of Fe, in dilute acid. Aqua regia may be used, but it is less reliable. The oxidation need not be made if the next group separation is to be made by NH_4SH .

^{3*} Holliday and Smoot, cf. Scott, "Standard Methods."

22. Division of the H_2S Group.—There are now from one to three precipitates, 2, and 2R and the recovered As or Mo. If the third precipitate is yellow, dispose of it by pouring NH_4OH on the filter. If it dissolves it is As_2S_3 . Record the fact and discard the filter and filtrate. If the precipitate is brown, it should be reserved. Mo will probably be found in precipitate 2. In case of doubt a fresh sample should be tested by the assay method. (See page 97).

2R will contain, generally, all the Sn from an ore treated by Method D, (15). It may also contain Sb, but not much else. 2 may contain any of the elements of the group. It will be more convenient to treat the two precipitates separately, combining the solutions afterward. They will be spoken of as one, and in most cases there will be but one.

23. Stock Alkali Solution.—Weigh about 15 grams of stick KOH in a 400 cc. beaker. The amount may be more or less, as it is not easy to break off an exactly even weight, so weigh what is put into the beaker, add an equal weight of K_2SO_4 , and add hot water equal to ten times the combined weights, giving a solution containing 5 per cent of each reagent. Pass H_2S into the solution for a few minutes to precipitate impurities. Let it stand over night or as long as possible before use. Decant the clear solution for use.

24. With the tube, a spatula or knife blade, assisted by not more than 20 cc. of water from the wash-bottle, transfer as much as possible of the precipitate to the beaker. Set the beaker under the funnel and pour stock alkali through the filter. If the precipitate is small, use 25 cc. If it is large, use 50 cc. Wash the paper once with hot water. Stir the mixture in the beaker to break up the lumps. Heat it almost to boiling, stir again and with pieces of paper wet with the solution and held by the tube rub down the sides of the beaker, so that every part of the precipitate has a chance to dissolve if it will. Heat again, fifteen minutes in all, and filter on a fresh paper suited to the size of the residue now insoluble. If the treatment has been successful, the residue will be perfectly black and will have no lumps, filtration will be rapid and the filtrate will be clear

yellow. Mark the filtrate 2B, being both combined if there are two. The residue from 2R, unless large, may be discarded, as it will contain only elements present in 2.

Put a fresh beaker under 2 and wash with hot water until acid H_2S water gives no precipitate in the last washing.

Failure to effect a separation of the sub-groups may be due to: (A) Acid in the precipitate. Add more stock alkali. (B) The presence of SnS . Stock alkali will not dissolve it. NH_4S_x dissolves it slowly and unsatisfactorily. After filtering away the alkali solution, return the residue to the beaker with 50 cc. of warm water, and add Na_2O_2 a little at a time with stirring until the precipitate turns black. It may dissolve completely. Now boil the solution for fifteen minutes, dilute, cool, make 1 per cent acid and precipitate Group 2 as before. After filtering and washing make the same stock alkali separation as before. The acid filtrate is discarded and the alkali filtrate combined with 2B.

The residue insoluble in alkali is marked 2A.

GROUP 2A—Ag, Hg, Pb, Bi, Cu, Cd

25. Mercury.—Transfer the residue 2A to the beaker with 20 cc. of water. Add 5 cc. of HNO_3 and boil two or three minutes. All but Hg and some free S will dissolve. Filter while boiling hot and wash with hot water into a 150 cc. beaker. Mark the filtrate Pb.

Transfer the black residue to a test tube, add 5 cc. of HCl and five drops of HNO_3 , and boil. Pour the solution away from the S into a small beaker, add 10 cc. of water and a few drops of a concentrated solution of SnCl_2 . If Hg is present, HgCl will precipitate, white at first and then turning grey and black through reduction to metal.

Note. If no HgS is present, the S residue is likely to be colored by some occluded sulfides of Cu or Bi. A small black residue, therefore, is no evidence of Hg, without a further test. Notice whether the size of the residue corresponds to the Hg found, to make sure that the other elements were dissolved in the dilute HNO_3 .

26. Lead.—To the HNO_3 filtrate add 5 cc. of H_2SO_4 , cover the beaker and boil down to fumes of SO_3 . Cool, add 35 cc. of water, mix well, boil and cool. Pb, if present, will form a heavy white precipitate of PbSO_4 , almost insoluble in dilute H_2SO_4 . If much Bi is present, some of it will be occluded by the Pb, and for a quantitative separation the precipitate should be given a special treatment, but the qualitative reactions will not be obscured by the occlusion. Filter and wash with cold distilled water. Mark the filtrate Ag.

Wash the precipitate back with hot water and dissolve it in a slight excess of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$. Precipitate PbCrO_4 as in (11).

Note. In case of doubt whether Bi is included in the PbSO_4 , add NH_4OH in excess to the $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ solution. Bi will precipitate at once, Pb only slowly. By filtering quickly a rough separation is possible. The filtrate can then be made acid with $\text{HC}_2\text{H}_3\text{O}_2$ and PbCrO_4 precipitated.

27. Silver.—Add a drop of HCl to the filtrate from PbSO_4 . Some Ag may have failed to separate by the Group 1 treatment, and it will be found here. Remove it by filtration and identify it by (4). Mark the filtrate Bi.

28. Bismuth.—To the filtrate add NH_4OH in slight excess. If a precipitate forms filter it and mark the filtrate Cu. If no precipitate forms, there may still be a trace of Bi which NH_4OH will not precipitate. Make the solution slightly acid and add a piece of solid ammonium carbonate, enough to make the solution alkaline before it entirely dissolves. Boil and set away to cool. Filter.

Sodium Stannite.—Prepare a few cc. of 25 to 50 per cent NaOH solution. Pour this into a small volume of SnCl_2 solution with stirring, until the precipitate which first forms has dissolved. This solution must be concentrated or it will not give the reaction for Bi, and it must be fresh, though it may be kept bottled tightly for a few days.

Pour a few drops of the Na_2SnO_2 solution on the precipitate supposed to be Bi. If Bi is present, it will turn black through reduction to metal. Other elements may be present, but they will not turn black. Sn or Sb may not have been entirely sep-

arated, and they will appear at this point. Cd may not dissolve entirely in the carbonate solution. Therefore, if a precipitate of considerable size is formed by carbonate and not by NH_4OH , it should be scraped from the filter and tested for Cd, and only a small part tested separately for Bi. In practice Bi and Cd do not interfere, because they hardly ever occur in the same substance.

Water Precipitation of Bi.—Dissolve the precipitate in a little 25 per cent HNO_3 and evaporate it to dryness. If it is very small, add five drops of HNO_3 and 1 cc. of water, and 0.1 gram of NH_4Cl . Warm until it dissolves and then pour in 100 cc. of hot water. For a large precipitate these proportions may be multiplied five times. Bi is precipitated as BiOCl , a white crystalline precipitate which forms shining waves when gently stirred, the "Watered Silk Effect." This is conclusive evidence of the presence of Bi, and a better way of estimating the quantity than the stannite test.

29. Copper.—The filtrate from the NH_4OH or $(\text{NH}_4)_2\text{CO}_3$ precipitation of Bi will be colored blue if Cu is present. This is a conclusive test if Ni has been completely separated by H_2S in the acid solution. In case of doubt a smaller amount of Cu may be identified by immersing a piece of bright Fe in the solution over night, after making it acid with H_2SO_4 and a few drops of HNO_3 . Cu will plate on the Fe with characteristic color at first, turning darker red and dropping off on standing.

30. Cadmium.—If Cu has been identified by the NH_4OH color, add solution of NaCN until the blue color disappears, and a slight excess. Pass H_2S . Cd will precipitate as canary yellow sulfide. The filtrate from the BiOCl precipitation by water may also contain Cd. Pass H_2S through it. In the acid solution, unless the acid is very dilute, CdS has an orange color.

If Fe has been used to identify Cu, it must be oxidized, precipitated with NH_4OH and filtered, the Cd being obtained in the NH_4OH filtrate as before.

31. Separation of As, Sb, Sn, Se, Te, and Mo.—If Mo is present, it will have been noticed during the previous precipitations, by

its incomplete precipitation in acid, and the blue color given to the filtrate by the reduced pentavalent Mo. The brown color of the precipitate afterward obtained is confirmatory. If these indications appear, it will be necessary to separate it before the other elements can be separated from each other.

If Mo is present, add Na_2O_2 to the alkaline solution 2B until the solution becomes colorless, and then boil for fifteen minutes. Make acid with H_2SO_4 . Do this cautiously, to see if any sulfides appear when the solution changes to the acid side. If they do, the solution must be made alkaline again by the addition of Na_2O_2 and boiled fifteen minutes. To the acid solution add $\text{Fe}_2(\text{SO}_4)_3$ in large excess over the Sn, Sb, etc., not counting the Mo, as indicated by the behavior of the original H_2S precipitate. Add NH_4OH in excess and filter, washing a few times with dilute NH_4OH . Saturate the filtrate with H_2S . In the presence of much Mo the solution will be red instead of yellow. Add acid in excess. MoS_3 will precipitate completely, chocolate brown. If a large precipitate appears, dissolve the $\text{Fe}(\text{OH})_3$ precipitate which contains the other elements, in H_2SO_4 , precipitate again with NH_4OH and test the filtrate for Mo. When the Mo has all been removed by repeated precipitations, dissolve the $\text{Fe}(\text{OH})_3$ again in H_2SO_4 , adding a little HCl if necessary for complete solution and precipitate As, Sb, Sn, Se, and Te with H_2S , filter them and wash thoroughly to remove the large amount of Fe, and proceed as in (32). Fortunately when Mo is found in minerals the other elements of the group are generally present only in traces, and qualitatively are hardly worth determining. The separations in (32) are in most cases made without considering the presence of Mo.

32. Add H_2SO_4 in excess to the alkaline sulfide solution 2B, precipitating the sulfides. Filter and wash free from Cl with 1 per cent H_2SO_4 . Wash back the precipitate and add from two to five grams of ammonium carbamate, which dissolves to $(\text{NH}_4)_2\text{CO}_3$. Stir to dissolve the salt and filter. Wash with water, twice. Acidulate the filtrate to precipitate As_3S_3 . The other elements remain undissolved in $(\text{NH}_4)_2\text{CO}_3$.

Wash back the precipitate of the other elements and dissolve them by adding Na_2O_2 with stirring. Boil fifteen minutes. Dilute to 100 cc. with hot water. Add $\text{H}_2\text{C}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$ until litmus paper is colored red, and two or three grams in excess. Stir to dissolve and pass H_2S . All the elements but Sn will precipitate. Filter and wash with 1 per cent H_2SO_4 containing no H_2S , making the last washing of beaker and filter with water. Mark the precipitate Sb and reserve it.

If there is much Sn, it will be convenient to make the $\text{H}_2\text{C}_2\text{O}_4$ filtrate alkaline with NH_4OH and then acid with $\text{HC}_2\text{H}_3\text{O}_2$. SnS_2 will precipitate white, turning to its characteristic brownish yellow on standing. Traces of Sn may not be found by this method. A more certain way is to add 10 cc. of H_2SO_4 to the solution, evaporate it to fumes, take up with water, adding 5 cc. of HCl if necessary to bring all but SiO_2 into solution, add dilute KMnO_4 solution to a pink to make sure that all $\text{H}_2\text{C}_2\text{O}_4$ has been destroyed, filter from SiO_2 , dilute to 200 cc. and pass H_2S . This, if all washings have been saved in the previous solutions of Sn, is an accurate quantitative method for small amounts of Sn, which can be ignited and weighed as SnO_2 .

33. Separation of Se and Te.—Dissolve the Sb precipitate in Na_4O_2 as before, boil, add enough HCl to make the solution slightly over 30 per cent acid in excess, boil, and pass SO_2 gas for a few minutes. Warm for an hour, if no precipitate forms before that time. If a black granular precipitate forms, either Se or Te are present. Filter them and mark the filtrate Sb. To distinguish between Se and Te, dissolve the precipitates in Na_2O_2 , boil, add 10 per cent excess of HCl , boil, add enough HCl to make the solution 80 per cent and pass SO_2 . Heat the solution to boiling and let it stand cold over night. Only Se will precipitate. Filter, dilute the filtrate with four times its volume of water, and repeat the SO_2 treatment. Te will precipitate.

The solution containing Sb is diluted to an acidity of not more than 10 per cent. H_2S will then precipitate Sb_2S_3 , red with a suggestion of orange.

GROUP 3

This group includes the elements in the filtrate from Group 2 which are precipitated by NH_4OH , Al, Fe, Cr, U, Ti; and to this we add V, because it is precipitated by U and partly occluded by $\text{Fe}(\text{OH})_3$, though by itself it is not precipitated by NH_4OH . The two solutions, 3 and 3R, must be kept separate in order to test 3 for Ni in the next group.

34. After boiling out the H_2S , oxidize as in (21). Add NH_4OH until a precipitate forms. Notice whether there is any indication of $\text{Fe}(\text{OH})_2$. If unfamiliar with its appearance, prepare some by adding NH_4OH to a solution of FeSO_4 . If the indication appears, add more aqua regia and boil again. Then add NH_4OH until the solution is barely alkaline, and boil until the solution no longer smells decidedly of NH_3 . Allow the precipitate to settle, filter and wash with hot water. Mark the filtrates 4 and 4R.

35. The precipitate will contain all the Fe, Ti, Al, Cr, and U. If the U is in excess over V, all V will be precipitated. If U is present and Fe is present in quantity, enough V will be included to give a test if it is present. In addition, Mn, Zn, Ni, Co, Mg, and Ca may be occluded to some extent. Wash the precipitate back, add one gram of Na_2CO_3 and one gram of Na_2O_2 and boil for ten minutes. This will dissolve U, V, Al, and Cr: U and V because they are soluble in carbonates, Al because it forms soluble aluminates with the alkalis, and Cr because it is oxidized to hexavalence and forms soluble chromate.

Filter and wash with hot water. Mark the filtrates A1 and A1R. Dissolve the precipitates in HCl . If there is a brown residue insoluble in dilute acid, put a fresh beaker under the funnel and pour H_2O_2 on the residue. If the residue dissolves instantly to a clear solution, Mn is indicated. Pb would behave in the same way if it were not completely separated before.

36. Basic Acetate Separation.—To the cold solution of the Fe precipitate add NH_4OH in slight excess. Form an estimate of the probable weight of the precipitate after ignition; by comparison with a known weight of Fe if necessary. For every 0.1 gram of precipitate there should be about 100 cc. in the final

volume of the solution. Dissolve the precipitate in as little HCl as possible. Add a 5 per cent NH_4OH solution a few drops at a time and finally dropwise, stirring after every drop, until the small precipitates formed by the drops of dilute NH_4OH dissolve with difficulty and the solution takes the dark reddish color which indicates a neutral solution of Fe. If a permanent precipitate forms through adding too much NH_4OH , dissolve it in HCl and approach neutrality again with the dilute NH_4OH .

Then add from two to three grams, according to the amount of precipitate, of $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3 \text{H}_2\text{O}$ dissolved in hot water, boil for one minute, and allow the precipitate to settle without getting cool. If there is any delay, keep the beaker on the water-bath. Prepare a rapid filter, amply large. For 200 cc., use eleven centimeters; for 300 to 400, use twelve and one-half centimeters. When the precipitate has settled, except a few flakes which may persist in floating about, take up the beaker in tongs or with a cloth, remove the rod carefully so as not to stir up the precipitate, and pour the clear solution through the filter without setting the beaker down. If the filtrate becomes slow before the beaker is empty, keep the solution hot on the water-bath until it has all been transferred to the filter. Wash out the beaker with boiling hot water as soon as there is room in the filter for the washings, and as soon as the level has fallen one centimeter from the top, wash around the top. Wash twice more after the filter has drained completely.

Fe and Ti are precipitated, with any Al that was not dissolved by the alkaline solution, free from Mn, Zn, Ni, Co, Ca, and Mg. If Cr were absent, this separation could be used in place of the NH_4OH precipitation, but trivalent Cr is incompletely precipitated in presence of $\text{HC}_2\text{H}_3\text{O}_2$. Mark the filtrates 4 and 4R, concentrate them by boiling, and add them to the other Group 4 solutions.

In this precipitate Fe can be recognized by its color without any other test. If only a trace appears, it may come entirely from impurities in the reagents, and a conclusive test requires a quantitative comparison between the sample and a blank de-

termination on the same quantities of reagents as are used with the sample.

Wash back the Fe precipitates, add 9 cc. of HNO_3 and stir to dissolve. Add a little Na_2O_2 . A yellow color, more intense than that of Fe, running to orange when the element is present in quantity, indicates Ti. A cherry red indicates V. The V may hide Ti. In such a case, divide the solution into halves and add HF to one half. This will bleach the Ti color, and by comparison of the two it can be seen whether both are present. If the division has been made, discard the half to which HF has been added, and to the other half add between 3 and 4 cc. of NH_4OH . If no division has been made add between 7 and 8 cc. Stir to complete solution. Add KMnO_4 to a pink and then FeSO_4 solution to bleach the pink. Add 10 or 20 cc. of reagent ammonium molybdate. A yellowing of the solution indicates P. A precipitate will form on stirring for ten minutes. The precipitate is 1.63 per cent P.

37. Precipitation of Al from Carbonate Solution.—To the carbonate solutions marked AI and AIR add 20 per cent HNO_3 until all of the normal carbonate has been changed to bicarbonate. This is shown by testing with turmeric paper until after successive additions of 1 cc. of acid the paper is no longer reddened by a drop of the solution. The change of litmus paper to purple is also an indication, but turmeric is easier to read. If Al is present in quantity it will precipitate before neutrality is reached. The precipitate is colorless and gelatinous. The certainty of this test depends on the completeness of previous separations, and assumes the absence of rare elements such as Ga, but for most purposes it is sufficient.

Allow the precipitate to settle and filter, marking the solutions U and U R. Al in the R portion is an indication of clay or feldspar in the gangue. Some of the P_2O_5 may have dissolved in the alkaline solution. If a fusion had been made of the NH_4OH precipitate with Na_2CO_3 or Na_2O_2 all the P would be found in solution and would be precipitated as AlPO_4 . Dissolve the precipitate in 9 cc. of HNO_3 , add 7 cc. of NH_4OH ,

dilute to 100 cc. with warm water and precipitate P with 20 cc. of ammonium molybdate solution.

38. Uranium and Vanadium.—To the filtrates U and UR add HNO_3 in excess, boil out the CO_2 and add NH_4OH in excess. If U is present it will be precipitated as yellow $(\text{NH}_4)_2\text{U}_2\text{O}_7$. If V is also present it will be precipitated with U. Filter and mark the filtrates Cr and CrR. Dissolve the precipitate in HNO_3 and test the solution with H_2O_2 for V.

Note. U will always be found in the soluble, and hardly ever in the residue insoluble in acid. V from the U mineral Carnotite is also soluble, but Roscoelite, containing no U contains insoluble V. Cr is more likely to be found in the R portion.

39. Chromium.—If Cr is present the solution will be yellow or orange. Add a few drops of H_2O_2 . Cr in quantity will give a momentary blue, fading to pale green or rose color. If V is present, it will show red. Add H_2SO_3 to decompose excess H_2O_2 , then NH_4OH in excess, and boil. Cr will yield an apple green precipitate of $\text{Cr}(\text{OH})_3$. The filtrate may be further tested for V.

GROUP 4

40. Manganese.—Reserve solution 4R, add NH_4OH and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ to solution 4 and boil. Mn, if present will produce a brown precipitate approximating MnO_2 . Filter and wash with hot water. Treat the precipitate with 10 per cent H_2SO_4 and then with H_2O_2 . If it remains insoluble in the acid and dissolves instantly in H_2O_2 , the presence of Mn is confirmed.

41. Ammonium Sulfide Precipitate.—Make 4R slightly alkaline and pass H_2S into it and the filtrate from Mn. 4R will give a large precipitate of NiS , which must be discarded. Zn, if alone in 4, will form white ZnS . Ni or Co will make the precipitate black. Filter and wash with NH_4SH , and boil the filtrates. If a black precipitate forms, filter again and wash with NH_4Cl solution. Mark the filtrates 5 and 5R, add HCl and boil out the H_2S .

42. Separation of Zinc from Nickel and Cobalt.—Put both papers and precipitates from 4 in one beaker, discarding those from 4R. Add 10 cc. of HNO_3 and 10 cc. of H_2SO_4 . Boil down to

fumes of SO_3 and add a few drops of HNO_3 at a time until the black residue of carbonaceous matter is destroyed. Cool, dilute, neutralize with NH_4OH and make acid not more than 0.2 per cent with H_2SO_4 . Pass H_2S briskly. ZnS alone will precipitate. Filter, add $\text{NaC}_2\text{H}_3\text{O}_2$ to the filtrate, and pass H_2S , which will precipitate Ni and Co. Filter, wash the precipitate back, add HNO_3 and boil until the precipitate is dissolved. Evaporate the solution to dryness. A green crystalline residue indicates Ni. A rose-colored deposit indicates Co. If both are present, they can be seen separately in different parts of the beaker. When one is seen clearly a precipitation test may be made for the other.

43. Nickel in Presence of Cobalt.—Take up the residue in water, add HCl and alcoholic solution of di-methyl glyoxime, and then NH_4OH to neutrality. A rose red precipitate confirms the presence of Ni.

44. Cobalt in Presence of Nickel.—Take up with water and HCl and make the solution 15 per cent acid with $\text{HC}_2\text{H}_3\text{O}_2$. Add nitroso beta naphthol, dissolved in 50 per cent $\text{HC}_2\text{H}_3\text{O}_2$. A bright red color, collecting to a red precipitate on standing, indicates Co. The reagent may produce a brown precipitate which does not contain Co.

GROUP 5

45. There may be two solutions, kept separate for the purpose of showing whether the Ca and Mg in the sample are there as silicates or as salts soluble in acid. Add NH_4OH in excess, boil and add to the boiling solution of about one gram of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$. Ca will precipitate, with Sr. Filter, dissolve the precipitate in HCl and test in the flame for Ca and Sr.

46. Cool the filtrates from Ca, add a solution of a phosphate and stir. If a precipitate does not form within a few minutes, add NH_4OH to 10 per cent of the volume and stir again. A precipitate may collect on standing over night. $\text{MgNH}_4\text{PO}_4 \cdot 6 \text{H}_2\text{O}$ is a white semi-transparent crystalline precipitate. It may appear on lines rubbed by the rod in stirring.

47. Barium is properly a member of this group, but on account of the insolubility of the sulfate it is separated in the beginning of the analysis.

GROUP 6

48. Sodium, Potassium and Lithium.—On account of the large mass of salts accumulated in the analysis it is inconvenient to separate Li and K, and impossible to identify Na, as salts of Na have been added. It is customary to test for these elements by regular quantitative procedure, based on the method of J. Lawrence Smith. Salts of these elements are easily identified by their distinctive flame tests. In the case of Na the test is so delicate that it is seen in almost any substance. Na in quantity is distinguished when a yellow of great intensity is produced by a minute amount of the sample, under conditions that did not yield such a color before the sample was added.

CHAPTER VII

DETERMINATIONS

Arsenic.—As is obtained in HCl solution as AsCl_3 by the Fischer distillation method. In small quantities up to one-tenth gram it is weighed as As_2S_3 . In larger quantities, particularly when obtained from materials free from Sb, which may contaminate the distillate, it is titrated with iodine solution.

Weighing as As_2S_3 .—If there is a possibility of Sb being present, make sure that the solution is at least 60 per cent HCl. Pass H_2S , and allow the solution to stand until the precipitate has settled. The best condition for filtering is when the precipitate is in loose flakes, not settled to a solid layer. In this condition policing is easier.

Prepare a rapid Gooch filter, and without drying pour in the solution, pushing the floating precipitate back so that it does not get into the crucible until toward the end of the filtration. Wash out the beaker and police with a camel's hair brush, as the precipitate sticks to rubber. Wash down the sides of the crucible once, remove it and wipe the outside, and lay it on its side in a shallow tray, such as a filter box, and dry it at 100° for thirty minutes. Allow it to cool in the open air until the crucible feels cold when touched to the forearm, and weigh.

Dissolve the As_2S_3 by passing NH_4OH through the crucible, dry as before, and weigh, taking the weight of the precipitate by loss. If there is free S precipitated with the As_2S_3 , a little of it will dissolve in the ammonia, giving high results. Generally this error is less than the losses of As during the distillation, and may be neglected. It is possible to dissolve the S away from the As_2S_3 by CS_2 , but the precipitate must be perfectly dry. Some chemists wash out the water with alcohol, and the alcohol with ether before applying the CS_2 , but in the writer's experience this does not get the precipitate sufficiently dry to allow the CS_2 to act perfectly. It is better to dry in the oven, then treat the precipitate with CS_2 , wash it out with ether, and dry again before weighing. The crucible may be weighed before the filtration or afterward. It is safer to do it afterward, for then it can be seen whether all the free S has been removed.

If some Sb has been precipitated with the As, it is possible to dissolve the As_2S_3 away from it by using a strong solution, 10 per cent or more, of $(\text{NH}_4)_2\text{CO}_3$, which does not dissolve other sulfides than those of arsenic.

Titration with Iodine.—Iodine solution. Decinormal.

Starch. Soluble starch, 1 per cent mixture, boiled and cooled.

Neutralize the acid in the distillate with NH_4OH , add a slight excess of HCl , cool in ice water or running water, add solid NaHCO_3 in excess, so that some remains undissolved for a moment after the solution becomes neutral, add 2 cc. of starch solution, and run in iodine solution at a regular rate, stirring vigorously all the while, until purple appears in the solution. Then add the solution dropwise until the blue appears.

A blank titration with these reagents and no As will give about 0.1 cc. of decinormal iodine.

A blank obtained by distillation may be large as 0.25 cc.

The solution should be standardized against pure sublimed As_2O_3 . This is easily prepared by placing some C. P. white arsenic in a flat-bottomed crucible in the bottom of a casserole, covering the casserole, and putting a Bunsen flame directly under the crucible. By a proper adjustment of the flame, the As_2O_3 will sublime on the sides of the casserole in dense crystals. These should be kept in a glass-stoppered bottle or in a dessicator. Weigh 0.25 gram of the As_2O_3 into a large beaker, dissolve it in a little concentrated NaOH , dilute to the volume of the neutralized distillate, add HCl in slight excess, neutralize with NaHCO_3 and titrate.

On account of the large end point correction, and also to guard against losses in distillation, it is more accurate to distil the standard under the same conditions as the sample. The assay of a white arsenic is merely obtaining the ratio between the figure obtained with it and that from an equal weight of pure As_2O_3 .

Antimony.—Sb is titrated with decinormal KBrO_3 , by a modification of Gyoery's method described by Low.⁴

⁴ Low "Technical Methods of Ore Analysis."

The Sb must be obtained in an HCl solution free from HNO_3 or other reducing agents. Cu and Fe may be present only in traces. A workable scheme, which permits the presence of as much as two grams of Pb or Sn, and a considerable amount of alkali salts, is as follows.

The solution should be brought to a volume of 75 cc. of 50 per cent HCl. If the sample is a suitable alloy, weigh from three-tenth to two grams into a 400 cc. beaker, add 75 cc. of HCl and warm on the top of a water-bath or oven at a temperature not above 80° until the evolution of H has ceased. Add 50 cc. of warm water.

Add KClO_3 a little at a time until free Cl is in excess and the precipitated Sb is dissolved. Boil down to 75 cc., and the solution is ready for the reduction.

If the sample is in a sulfide solution, evaporate it if necessary to 75 cc. of warm solution, add an excess of KClO_3 and 50 cc. of HCl, stir until all sulfides are decomposed, and boil down to 75 cc.

A sample of pure metallic antimony, or the standard, is more easily dissolved by adding 75 cc. of hot water, 50 cc. of HCl, and excess of KClO_3 , and stirring occasionally to keep cakes from forming, until solution is nearly complete, and then boiling.

Reduction of Sb.—To the cold solution, 75 cc. of 50 per cent HCl, add 40 cc. of H_2SO_3 solution of 1.03 specific gravity or stronger. Stir well and leave the rod in the beaker. Boil down briskly to 75 cc. and cool. Add 20 cc. of the H_2SO_3 and 60 cc. of HCl, stir, and boil down to 75 cc. again. In the meantime boil a mixture of 40 per cent HCl, and when the sample has reached about 75 cc. add 50 cc. of the 40 per cent HCl. A well made graduated cylinder can be used safely to measure the hot acid.

Finally boil down to 75 cc., add 100 cc. of boiling water and titrate at once. The titration is conducted as follows.

Decinormal Potassium Bromate.—Methyl orange, one gram per liter in water.

Add one drop of methyl orange. Run in the bromate solution from a burette in a regular stream with vigorous stirring until the red shows signs of fading. Add another drop and proceed until fading is noticed again. Add a third drop and continue the titration dropwise until the pink entirely disappears. One-tenth cc. is about the right subtraction for the end point.

After a little practice to get accustomed to the rate of fading of the methyl orange, this method of titration is rapid and easy. Errors are due more to lack of attention to the boiling than to any other cause. The chemist is always aided by having seen the Sb before titration, either as sulfide or as precipitated metal during solution.

The solution is standardized against an analysed sample of metallic antimony. It is difficult to obtain a sample purer than 99.5 per cent, but the impurities do not interfere with the titration, needing only to be counted in measuring the Sb present.

Small amounts of Se and Te precipitated during the reduction will dissolve on boiling and do not interfere with the titration.

As, if reduced, is expelled. If not reduced, it does not interfere, so no attention need be paid to it if the scheme is followed exactly. The writer has found as much as 0.12 gram of As after an Sb titration, separated it, and afterward obtained the same figure for Sb.

Low says that Fe interferes very little. The writer has found that less than 0.003 gram of Fe may be disregarded. More should be separated, as it may make large errors.

The advantage of this method over the many others available is mostly in its freedom from the interference of As, Se, and Te.

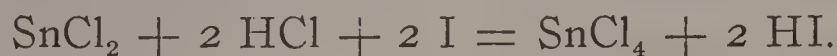
Tin.—Sn is weighed as SnO_2 or titrated with iodine solution.

The gravimetric method is useful for the determination of amounts of Sn so small that they might be confused with the end point correction of a titration, or which have been obtained in the course of a qualitative test.

It can be made part of a nearly complete analysis of an alloy on one weighed portion. The details of this method consist principally in the handling of the other elements which are occluded

with Sn in precipitation. The method will therefore be discussed under Separations.

The titration method follows the reaction



Standard solution, decinormal iodine.

Indicator, 1 per cent starch solution.

Reducing element, a piece of nickel 0.015" x 2" x 6" made into a loose roll, as large as can be put into the flask, through which liquid can circulate easily.

Apparatus, a 500 cc. Erlenmeyer flask with a "sulfree" rubber stopper and tube as shown in Fig. 14. The diameter of the outlet tube should be about 3.5 millimeters and the capacity about

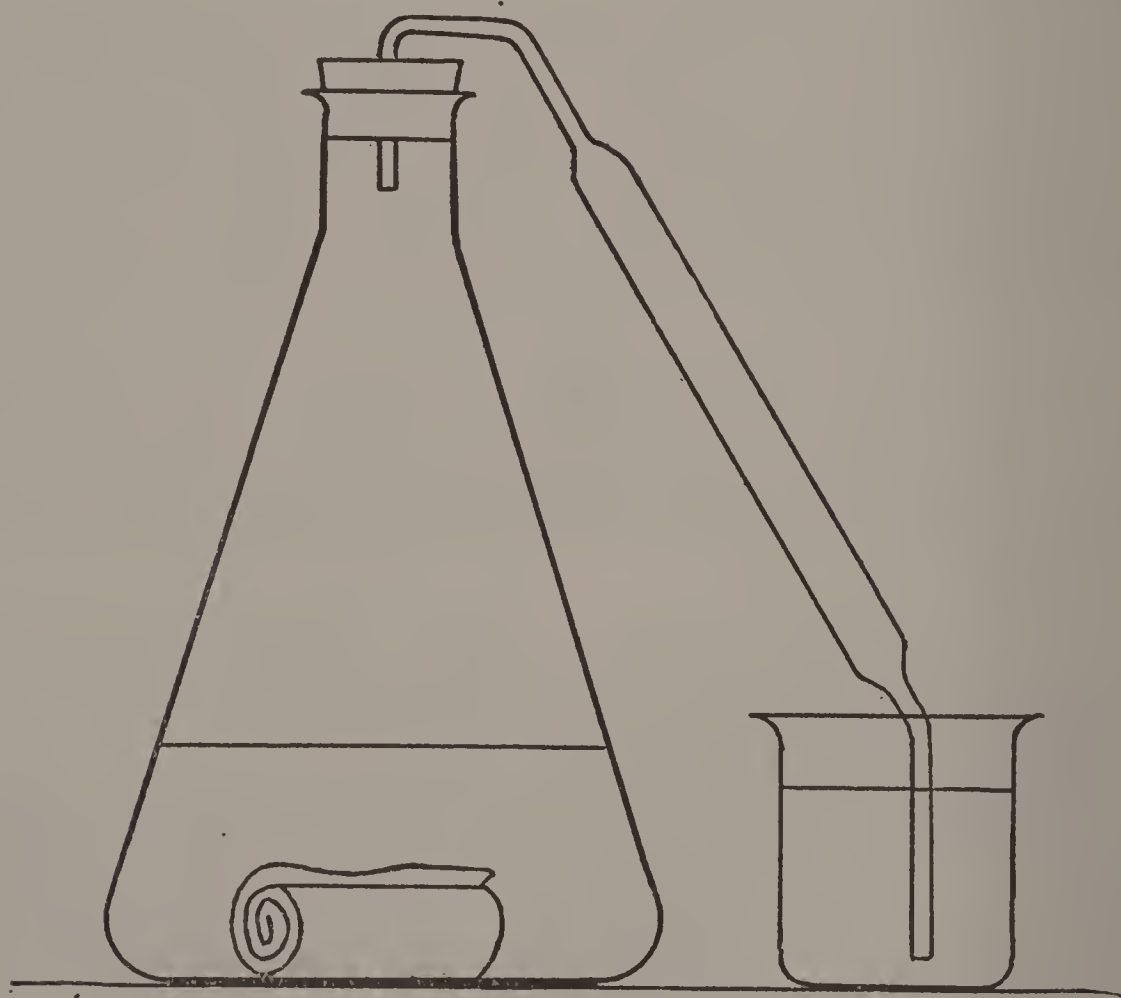


Fig. 14.

12 cc. to insure quiet action of the carbonate solution. This form of outlet tube was suggested by Charles G. Snyder, who used a bent pipette.

The Sn should be a soluble form free from oxidizing agents which cannot be boiled out, such as HNO_3 . Not more than 0.005

gram of Cu should be present. The effect of Cu is to precipitate as metal and dissolve during the titration, giving high results. As in the traces usually found in engineering materials does not interfere, though in quantity it is said to deposit on the nickel and carry some Sn with it.

The iodine solution is standardized against pure tin. Weigh different amounts up to 0.3 gram into flasks, add 15 cc. of H_2SO_4 and heat strongly until solution is complete. Cool, dilute, add from 200 to 250 cc. of water and 30 cc. of HCl, put in the reducing roll, connect the stopper and tube and heat to boiling. Keep it gently boiling for forty-five minutes. Place a small beaker containing boiling water and a few grams of NaHCO_3 on the hot plate and insert the end of the outlet tube without stopping the boiling. Make sure that all air is expelled from the tube, remove beaker and flask without allowing air to enter, and cool the flask in running water or ice water. As soon as the carbonate solution has ceased to oscillate, remove the stopper, add 2 cc. of starch solution and run in the standard iodine in a regular stream with as much stirring as possible by rotating the flask obliquely without breaking the surface of the liquid. As the Ni forms a green solution, it is of advantage to hold the flask above a well illuminated white paper, so that the blue of the starch can be seen. When the blue appears the end is near. A purple or pale blue that remains after mixing is one drop from the end.

An end point subtraction of about 0.2 cc. is required.

Alloys which can be decomposed by H_2SO_4 alone, and which contain no interfering impurities, such as solder, type metal, etc., may be run in the same way as the standard. Instead of H_2SO_4 , an equivalent of HCl, amounting to 65 cc. in all, may be used, as in acidulating the solution from a sodium peroxide fusion.

Lead.—Pb is weighed as PbSO_4 and PbCrO_4 . The titration methods take almost as much time as the gravimetric, and are less accurate.

Having the Pb in solution, preferably in slightly dilute HNO_3 , add sufficient H_2SO_4 to give excess over all bases present; preferably 10 cc. for a 400 or 600 cc. beaker, and 0.3 gram or more of Pb, and 5 cc. or less for smaller beakers and less Pb. The

acid should be enough to cover the bottom of the beaker. Cover the beaker and boil down to fumes of SO_3 . A drop of HNO_3 which hangs on the under side of the lid causes no appreciable error. Cool, add from six to eight times as much water as there is acid, mix well to prevent explosion, and boil until all soluble salts are dissolved. Cool and let stand for thirty minutes or more. If no impurities remain insoluble, and the filtrate is not needed, the Pb may be weighed as PbSO_4 . Otherwise it is more convenient to convert it to chromate.

Lead as Sulfate.—Prepare a Gooch crucible filter, dry and weigh it. Filter and wash the precipitate with 1 per cent H_2SO_4 , transferring all of it to the crucible. Wash out the acid with absolute alcohol, dry, heat almost or quite to redness, cool and weigh. The theoretical factor is used.

Lead as Chromate.—Ammonium acetate solution. Mix eighty volumes of NH_4OH , one hundred of water, and seventy of glacial acetic acid. Twenty-five cc. of this solution, which fills a nine centimeter filter, is enough for 0.5 gram of Pb. Larger amounts, particularly if in cakes or flakes instead of grains, may require more.

Potassium Dichromate. Cold Saturated Solution.—The presence of insoluble SiO_2 , or a little hydrolysed Sn, may be disregarded, as they carry no Pb and remain insoluble in acetate.

If there is enough Ca, Bi, or Sb to contaminate the sulfate precipitate, they will interfere with the chromate determination. Such cases will be discussed under Separations.

Having the PbSO_4 ready to filter, prepare a small rapid filter with a narrow-stemmed funnel. Nine centimeters is generally the best size. The corner should be torn off if there is no fine residue of pulverized quartz. If there is, the paper should be left entire and the column secured by a little pulp poured around the edges of the paper. Filter, wash the precipitate into the filter but do not police the beaker. Wash the top of the paper free from acid, testing by touching the paper with the tongue.

It is useless to test the filtrate, as water causes the PbSO_4 to hydrolyse, not dissolving Pb but making the washings acid.

With hot water in the wash-bottle wash back the precipitate, holding the filter with the inside flap downward, and folding the flap back with a knifeblade to wash under it, so that all of the precipitate is removed from the paper. Before washing back warm the lower edge of the funnel by playing hot water on it. This will keep the precipitate from sticking to it.

Fill the paper once with the hot acetate solution, adding more if the precipitate is large and does not dissolve quickly. If the precipitate is fine it will dissolve with stirring only. If it is caked or has flakes it should be warmed but not boiled, with occasional stirring, until all Pb is dissolved. If anything remains which is not recognized as a residue which will not contain Pb, such as sand, further work is necessary, which will be discussed under Separations.

When the Pb is all dissolved, filter and wash once with hot water, receiving the filtrate in a 400 cc. beaker for 0.5 gram or more of Pb and smaller sizes in proportion.

Pour 2 to 5 cc. of acetic acid into the filter and fill it with hot water, so that all of it is washed with the dilute acid. This is to dissolve any basic lead acetate which the hot water may leave in the paper. Wash three or four times more with hot water. Dilute the filtrate to 300 cc. or less in proportion to the amount of Pb, with hot water. Add the dichromate solution from a pipette with stirring until the color of the solution obscures the pale yellow of the precipitate, making it appear slightly orange. Ten cc. is enough for 0.5 gram of Pb. Warm on the water-bath with occasional stirring until after stirring the precipitate settles quickly, leaving a clear solution. Cool in ice-water or let stand over night.

Prepare a weighed Gooch crucible. Filter the cold solution, using the full force of the suction, transfer the precipitate to the filter and police the beaker at once. Wash the sides of the crucible with hot water and flood the precipitate twice. Dry the crucible in an oven which heats gradually, reaching 600°, or such a temperature that parts of it show red, in from fifteen to thirty minutes. If no oven is available, place the filter in an ordinary crucible over a Bunsen flame and heat gradually until in the

same time the outer crucible shows red in spots. Cool in open air and weigh.

As PbCrO_4 contains a little water, it is necessary to use an empirical factor, somewhat lower than theoretical. The writer has found a factor of 0.6381 for the Gooch filter dried at 100° , and 0.6391 when dried at 600° .

Small amounts of PbCrO_4 may be filtered on paper and ignited. If the filter is carefully roasted the error will be inappreciable.

Bismuth.—Bi is weighed as BiOCl . It must be in solution free from other acids than HNO_3 and HCl . Small amounts of elements which do not easily hydrolyse, such as Pb and Cu, may be present, but Sb and more than traces of Fe must be absent.

Evaporate the solution to dryness. If the residue appears to contain only a few milligrams of Bi, add six drops of HNO_3 and 2 or 3 cc. of hot water and warm to dissolve. Disregard a small cloudiness. Add about 0.2 gram of NH_4Cl and warm again. The residue should now dissolve. If it does not, further separations are necessary.

Now add 300 cc. of hot water. Stirring is not necessary. The precipitate should form in glancing crystals, giving the "watered silk" effect. Cool, filter on a weighed Gooch crucible, dry at 100° and weigh as BiOCl . The theoretical factor is used for small amounts.

For larger amounts, more than 0.01 gram, the same procedure is followed, but all the quantities are increased. For 0.2 gram of Bi there should be enough acid to keep a clear solution at 20 cc. volume. It is best to add about fifteen drops of HNO_3 and half a gram of NH_4Cl and a few cc.'s of hot water, and if a milky precipitate forms add enough acid to dissolve it, then NH_4OH until a slight cloudiness forms, and then HNO_3 drop by drop until the solution is clear again. Now add a little more hot water, and if no precipitate forms, dilute to 300 cc.

If there is as much as 0.5 gram of Bi, it should be kept in solution up to 50 cc. or more, and then largely diluted. With care and good luck a crystalline precipitate can be formed with large amounts of Bi, but unless the precipitate is formed at so

great a concentration as to occlude the other elements, the results will be accurate with a light cloudy precipitate, though filtration will not be so easy.

For large amounts of Bi an empirical factor should be established.

Copper.—The most accurate method for the determination of Cu is the electrolytic. The details of the method must be worked out by each laboratory to suit its requirements for time and expense, and its available apparatus and current. Where a few determinations are to be made quickly, the rotating anode or other stirring device is used. Where economy of labor is important, it is best to use fixed electrodes with deposition period of several hours, preferably over night.

The best electrolyte is a mixture of HNO_3 and H_2SO_4 . The amount of HNO_3 depends principally on the amount of Cu to be deposited. HNO_3 is converted to NH_4OH during the electrolysis of a Cu solution. In plating one gram of Cu as much as 2.45 cc. of reagent HNO_3 may be reduced to NH_4OH .⁵ It is necessary to have enough HNO_3 to last through the electrolysis, and enough volume of electrolyte to dilute the acid, so that the concentration may not prevent deposition.

The amount of H_2SO_4 depends more on the volume of the solution and the amount of current, as it is not altered during the electrolysis, except to increase through the disappearance of the Cu ions. The object of its use is partly to increase the conductivity of the solution and partly to prevent the deposition of other elements.

Nitrites may be present when H_2SO_4 is used. When only HNO_3 is used, even the fresh reagent must be boiled before electrolysis to free it from HNO_2 .

An example of a satisfactory electrolyte is two grams of Cu in 175 cc. of solution containing 6 cc. excess HNO_3 and 10 cc. H_2SO_4 , with a cathode of about 100 square centimeters plating surface and 0.5 ampere for twelve to fifteen hours. But there are so many factors to be considered that only experiment on a particular equipment will show what solutions should be used

⁵ Luckow. *Zeit. Anal. Chim.*, 19, 11, 1880. Easton, *J. A. C. S.*, 25, 1042.

with it. Such books as Smith's "Electro-Analysis," and Heath's, "Analysis of Copper," give valuable data and advice.

The best cathode for slow deposition is a cylinder made of perforated sheet platinum. This is easily kept clean by polishing occasionally with a rotating steel bristle brush, so that its weight changes very little from day to day. The perforations permit the circulation of the solution almost as well as gauze under the slight impetus of the bubbles rising from the anode, and keep down the tendency to "sprout" or form arborescent extensions.

The best anode is the largest that can be conveniently placed inside the cylinder without danger of touching on slight movement. A basket is better than a coil, and a coil is better than a straight wire. A helically coiled wire, occupying a cylindrical space half the diameter of the cylinder, is good compromise. It distributes the current evenly the length of the cathode.

HCl in more than traces prevents the formation of a good dense deposit, though it is possible by careful measurement to precipitate Ag with dilute NaCl without interfering with the Cu deposit from the filtrate.

Se and Te are as easily deposited as Cu, and must be absent or accounted for, to reverse the military phrase. Ag and Bi are also deposited with Cu and prevent the formation of a good deposit. Sb, As, and Pb in small quantities do not interfere if there is a sufficient volume and concentration of H_2SO_4 . Sn does not interfere except mechanically when there is a large precipitate. Fe in large quantities sets up oxidizing reactions which prevent deposition.

Copper by Color.—In small quantities Cu is conveniently determined by color comparison. A standard solution should be kept containing one gram of Cu per liter, or one milligram per cc. The Cu for comparison is generally obtained as CuS. The precipitate should be ignited in a small porcelain crucible, preferably with a flat bottom and vertical sides. The ignited residue is dissolved in HNO_3 , evaporated to a few drops, diluted slightly, and NH_4OH in excess added. A similar crucible is used for the standard. NH_4OH is put into it and the standard

copper solution run in from a burette until the color is matched at the same volume as the sample.

Sometimes a small amount of impurity alters the color of the solution to green or purple. A little ferric oxide rouge added to the standard will give it the purple cast to match, and a trace of K_2CrO_4 will produce the green. It is often impossible to make any comparison unless this alteration is made, as the small precipitate is likely to be impure. The effect of a white precipitate or residue is matched by an inert white powder such as ground quartz.

The crucible is the best container for small amounts of Cu from 0.0001 to 0.002 gram. For larger amounts a comparison tube, short and wide enough to stand alone, is convenient. This tube should be just large enough to admit the cathode, so that small dark deposits may be dissolved and compared with a minimum of solution.

Cadmium.—A good general method for the determination of Cd is electrodeposition from a cyanide solution. Zn must be absent. Cu, if present, may be determined afterward by color and the weight deducted. After the separation of Cd from other elements, it is obtained as CdS on a paper filter. The paper is destroyed and the Cd dissolved by treatment with HNO_3 and about 5 cc. of H_2SO_4 . After destroying the organic matter, the cover of the beaker is removed and the free H_2SO_4 expelled. Take up with water, add a gram of NaCN in solution, transfer to an electrolysis beaker and electrolyse with a very low current, not more than $N.D._{100} = 0.1$ ampere. The deposition is rapid, two hours with fixed electrodes being enough for small quantities.

By careful adjustment of acidity to current, or by the use of limited voltage as directed by Smith,⁶ Cd may be determined in presence of Zn, so that the partial separation of that element in the analysis of spelter is enough. For this purpose it is necessary to expel all HNO_3 and its decomposition compounds by repeated evaporations of the H_2SO_4 solution to fumes of SO_3 .

⁶ Smith. "Electro-Analysis."

Cadmium as Sulfate.—In the absence of electrolytic apparatus, the H_2SO_4 solution after concentration and the expulsion of most of the acid may be transferred to a weighed crucible, evaporated to dryness and heated sufficiently to drive off all excess H_2SO_4 by manipulating the crucible in the flame. The theoretical factor for CdSO_4 is used. If Cu is present an error may be introduced by the partial decomposition of its sulfate. It is better, therefore, to separate Cu by the precipitation of CdS from the cyanide solution before the determination.

Iron.—So much has been written about the Fe determination that further discussion would seem to be superfluous. A few hints and reminders, however, may not come amiss.

It is rarely safe to determine small amounts of Fe by weighing the oxide. Too many impurities are likely to be included in the precipitate. Instead it is better to use a small reductor made of a 25 cc. burette or a tube of the same size. The form shown in Fig. 15 is easily made from tubing of any size. By the use of blanks on the reductor as corrections on determinations, and dilute KMnO_4 , the error of the determination may be kept as low as 0.0002 gram.

It should be remembered that the filtration of an acid solution produces more or less sugar from the paper, and also that traces of HNO_3 produce comparatively large reducing effects on passage through the reductor. Greater accuracy, therefore, is obtained by evaporating the H_2SO_4 solution to fumes and while hot adding a small crystal of KMnO_4 before passing through the reductor.

As most rocks contain traces of Ti, some account needs to be taken of its presence in ore analysis. Traces of Ti have no appreciable effect on the KMnO_4 titration of Fe, as Ti is easily oxidized by dropping through the air from the reductor to the flask. If much Ti is present, the H_2S reduction is convenient. Fresenius⁷ describes the method carefully. As a precaution, it is useful to test the solution with KCNS to see if the Fe is reduced before boiling out the H_2S . KCNS ordinarily contains some oxidizing material which will give a reaction for

⁷ Fresenius. "Quantitative Chemical Analysis." Vol. I.

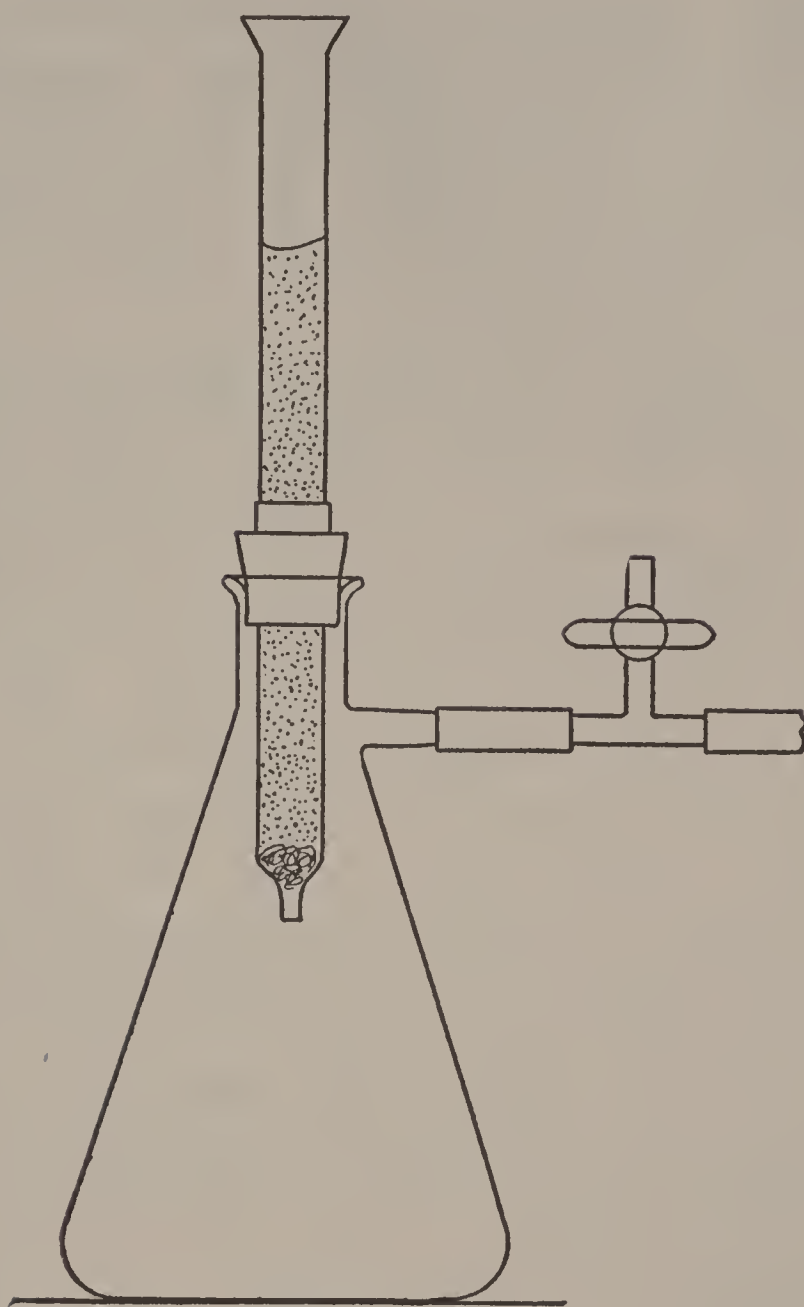


Fig. 15.

ferric iron even when the Fe tested has been entirely reduced. In order to get negative results for trivalent Fe, it is necessary to treat some KCNS solution with SO_2 , and boil out the excess, before using it. Commenting on Fresenius, the apparatus shown in Fig. 14, using a bicarbonate solution, is convenient for boiling out H_2S and cooling the solution.

Aluminium.—Al is determined by weighing its oxide. In most cases it is necessary to weigh other elements with it; Fe_2O_3 , TiO_2 , and P_2O_5 . The treatment of this mixture will be discussed under Separations.

Al_2O_3 requires the full heat of the blast lamp for its complete dehydration. Such a temperature will reduce Fe partly

to Fe_3O_4 . Ordinarily a balance of errors is obtained by a moderate blast heat with thorough oxidation. Fortunately highly accurate determination of Al are rarely necessary.

Chromium.—Small amounts of Cr are determined by weighing the oxide, Cr_2O_3 and larger quantities by reduction from hexavalence to trivalence.

The method of reducing the chromate by ferrous salt and then titrating the excess ferrous salt with KMnO_4 is described by Scott.⁸ The greatest difficulty in the use of this method is in distinguishing the end point of pink through the green of the reduced Cr. In the laboratory of Lucius Pitkin, Inc., an old carbon filament lamp, which gives a reddish light, is placed behind the beaker in a rather dark room. This makes the green almost invisible, and shows the pink clearly.

The determination of the end point correction is another difficulty. A fairly good way is to allow the end color to fade entirely after a titration and then to add more KMnO_4 to a pink. By testing several which have stood for different lengths of time, a fair approximation to the proper correction can be obtained. This, however, will hold good only for about the same amount of Cr. On account of the back titration, the ordinary algebraic solution from standard chromate is too complicated for practical use.

Vanadium.—V is reduced from V_2O_5 to V_2O_4 by repeated evaporation with HCl. Other elements such as Cr and Fe do not interfere, so that it is possible to assay most ores for V without separations.

Having the V in solution in either HCl or H_2SO_4 , HNO_3 being absent, add KMnO_4 solution in excess to make sure that no other substances which will reduce KMnO_4 remain. Then add H_2SO_4 enough to total 20 cc. and HCl to total 50 cc. Evaporate at a low temperature on the hot plate uncovered to incipient fumes of SO_3 , cool, add a little water and 25 cc. of HCl and repeat. For samples high in V a third evaporation is advisable. Finally cool, dilute to 200 cc., heat on the water-bath to dissolve

⁸ Scott, "Standard Methods."

all cakes and crystals of $\text{Fe}_2(\text{SO}_4)_3$, and titrate hot with KMnO_4 to the first appearance of pink throughout the solution.

Reduction of Vanadium by Sulfur Dioxide.—V may be reduced completely to tetravalence by the addition of a small excess of SO_2 to the H_2SO_4 solution. The excess is boiled out and the solution titrated hot. The operation is best carried out in a Florence flask half full. Paper moistened with fuchsin solution will bleach in the steam containing SO_2 . Or the steam may be smelled occasionally and the solution boiled for fifteen minutes after the SO_2 can no longer be detected.

Electrolytic Reduction of Vanadium.—Perfect reduction of V to V_2O_4 is obtained by passing an electric current through the H_2SO_4 solution. This method is suitable for accurate work on high grade material.

Uranium.—Gooch and Pulman's method is used, in which the sulfate solution is passed through a reductor and titrated with KMnO_4 .⁹

Some of the author's recommendations for the use of the reductor seem to the writer unnecessary. It is important not to allow air to pass through the reductor, but the acid may be diluted as low as 2 per cent, and the solution need not be hot, thus avoiding all trouble from H in the reductor. If the flask be shaken for one minute and the solution titrated in the flask, as concordant results as are possible are obtained. On account of the high atomic weight of U, KMnO_4 about 0.05 N should be used.

It is necessary to establish a blank correction by going through all the operations of separating the elements which interfere; particularly Fe and V, if they are found in the samples to be analysed. The corrections for different materials may vary as much as from 0.3 cc. to 0.8 cc. A fixed scheme should therefore be used with its correction for each type of sample. The common types are, 1, Alloys; 2, Carnotite ores containing V; 3, Pitchblende, containing no V; 4, Uraninite, manufactured products and concentrates high in U.

Zinc.—Low's method is recommended.¹⁰ The writer pre-

⁹ Gooch. "Methods in Chemical Analysis."

¹⁰ Low. "Technical Methods of Ore Analysis."

fers a few variations. Uranium acetate gives a slightly better end color than the nitrate. A rubber-tipped rod is convenient for stirring, as there is less danger of breaking the beaker, and less wear on it. Lifted horizontally out of the beaker it will hold enough solution for the test.

It is convenient to divide the solution into two equal portions in beakers of the same size before titrating, and to keep one-half hot while titrating the other roughly. Then all but enough to account for 1 cc. of the standard solution is poured from the original beaker into the extra one and solution measured in to within a few cc of the expected end. Then the end is approached 1 cc. at a time, and when the color is obtained, the solution, now spent, is poured into the original beaker without washing, and the titration finished 0.1 cc. at a time.

The extra beaker can then be used without rinsing for the next titration.

Before titrating, the solution should not be heated long enough to expel all the H_2S . Otherwise the chlorate, which is not all destroyed during the separations, will begin to act, causing a green color and high results. A blue color is produced by a little Fe, but this will disappear before the end, and does not produce an error. Indeed, it is a useful aid to the titration. Some use it as an indicator.

In the separations, the writer prefers 250 cc. beakers to flasks. They allow more rapid evaporation and are easier to police.

In filtering, no stirring rod is necessary. The policeman is used for the first pouring. The sides and bottom of the beaker are then rubbed. By this time the filter is empty. Fill it again, rinse and remove the policeman, and proceed to the next beaker. A third pouring will empty the beaker, and the drop can be touched off on the edge of the filter.

The leaching solution may contain ammonium persulfate instead of bromine water. Enough is used to give 0.25 gram per sample.

Low uses only one separation. This is enough for most ores. Occasionally, an ore turns up in which two separations are necessary, so that it is safer to use two in all cases of doubt. For the

second separation, the original beaker is placed under the funnel, the paper opened at the bottom with a metal point and the bulk of the precipitate washed through. 10 cc. of HCl poured around the paper with one washing will clear the paper. The HCl is used for its superior solvent effect. It is evaporated to dryness, replaced by HNO_3 , and the KClO_3 treatment etc. repeated. If the sample needs no HCl treatment it is not likely that a second separation is necessary, though for safety one may use HNO_3 to dissolve the precipitate, adding the KClO_3 when the solution has evaporated to 5 cc, with less work.

Nickel and Cobalt.—The electrolytic method is the most accurate, and in many cases is all that is necessary, the two metals being reported together.¹¹

If there is a considerable amount of Co, so that the error of the differential method is not too large in proportion to it, it is best to dissolve the two metals from the cylinder and determine Ni as glyoxime.¹² If there is but little Co, it is best to determine it by nitroso beta naphthol and take Ni by difference.¹²

This method as described is troublesome, as the reagent precipitates when it is added to the main solution, leaving the success of the Co precipitation in doubt. If the solution containing the sample be made 15 per cent acid with acetic acid, the reagent itself will not precipitate, and the Co precipitate can be clearly seen. This makes the method a good qualitative test for Co, and the quantitative determination is more convenient and reliable. The solution should stand for at least an hour before filtering, as the precipitate collects slowly. If it is allowed to stand over night, a small brown precipitate of the reagent may form in the absence of Co, which is easily distinguished from the flesh red of the Co precipitate.

Calcium.—Ca in small amounts is best determined as oxide by ignition of the oxalate at blast temperature. In larger amounts, or where the small error of the end point is negligible, the oxalate should be titrated.¹³

¹¹ Smith, "Electro-Analysis." Scott, "Standard Methods." Low, "Ore Analysis."

¹² Scott, "Standard Methods." Low, "Ore Analysis."

¹³ Fresenius, "Quantitative Analysis." Scott, "Standard Methods." Low, "Ore Analysis."

If the titration method is to be used, it is not necessary to polish the beaker, but it is necessary to wash both beaker and rod several times with hot water to make sure that the adhering crystals are washed free from the precipitant.

It is best to use an empirical factor based on the particular method of precipitation and washing. In the laboratory of Ledoux & Co., the iron value of the permanganate is multiplied by 0.5048 instead of the theoretical 0.5020.

CHAPTER VIII

SEPARATIONS

Tin from Other Elements.—Having the Sn in the form of SnS_2 mixed with other sulfides, filter with pulp and wash with 1 per cent H_2SO_4 , by decantation (page 73) if the size of the precipitate or the quantity of the lower group elements seems to make it necessary. Treat the precipitate with stock alkali solution (page 64) and filter. Reserve the filtrate. If the residue is very small it may be assumed that the separation is complete. If it is large, some Sn will certainly remain with it. Put paper and residue back into the beaker, add 10 cc. of H_2SO_4 and destroy the paper with HNO_3 (page 74). Cool, dilute, boil, and if PbSO_4 appears, the solution being otherwise clear, cool and filter. If a white milky residue appears, with or without PbSO_4 , add just enough HCl to dissolve it by boiling.

Having a clear solution, dilute to about 150 cc. and pass H_2S into the hot solution, without regard to whether Pb is precipitated or not. Filter and treat the precipitate with stock alkali as before, using as little as possible to make the mixture decidedly alkaline. Combine the two alkaline solutions, which should contain all the Sn and Sb, but perhaps not all the As. By taking care of the acidity and temperature of the solutions, the alkali insoluble elements may also be completely separated, with the exception of Cu, a little of which will afterward be found with the Sb.

In case the residue insoluble in alkali cannot be washed with hot water without running through, dilute NH_4S_x may be used. In some cases, as where there is much Bi, it may be necessary to use NH_4SH instead of stock alkali. The objections to using this reagent in all cases is that Cu is somewhat more soluble in it and the quantity of S and of salts admitted is larger.

Having all the Sn in alkaline solution, add Na_2O_2 a little at a time with stirring until the solution becomes colorless. Boil for fifteen minutes and add solid oxalic acid to the hot solution until litmus paper turns red, and three to five grams in excess. As the method is used only for small amounts of Sn, this amount

of oxalic acid is generally enough. If a slight precipitate forms from incomplete decomposition of the sulfides, boil until all SnS is dissolved. Dilute to 100 or 200 cc. with hot water and pass H_2S to precipitate all Sb and As. In the absence of HCl Sn has no tendency to reduce and form SnS . Filter and wash with 1 per cent H_2SO_4 containing no H_2S . The precipitate contains all the Sb, which may be determined by titration.

The filtrate contains the Sn. The precipitate may, if it is large or if there is much Sn in the sample, contain a little Sn. This may be separated by washing the precipitate back and dissolving it with Na_2O_2 and repeating the oxalic acid separation, using in this as small volumes and as little reagent as possible.

Having the Sn in oxalic acid solution, free from all other elements of its group, there are two methods of getting it out. One method¹⁴ is to add NH_2OH in excess, pass H_2S if necessary to get the Sn into solution, filter away any FeS that may appear, and make the solution acid with acetic acid. Sn will separate at first white, afterward assuming its natural color. Walter Spuhr and the writer have both found that this method gives low results, but when the tests were made there may have been losses by volatilization of SnCl_4 . Further experiments are necessary. The other method¹⁵ the writer can vouch for. That is to add enough H_2SO_4 to the oxalic acid filtrate to keep all bases in liquid form and boil down to fumes, destroying all oxalic acid. Take up with water, add KMnO_4 to a slight pink, then if necessary add a little HCl to dissolve Sn, filter from SiO_2 , and precipitate SnS_2 . The precipitate is filtered, washed with 1 per cent H_2SO_4 and weighed as SnO_2 . This is preferable when the determination is to be both qualitative and quantitative. If Sn is known to be present in quantity, the solution after fuming may be transferred to a flask, reduced with nickel and titrated with iodine.

Separation of As from Other Elements.—By distillation of AsCl_3 arsenic can be separated in convenient form for determination from all inorganic materials.

¹⁴ Crooks. "Select Methods in Chemical Analysis."

¹⁵ Fresenius. "Quantitative Analysis."

Most of the apparatus described is unnecessarily complicated. When As is trivalent it distils readily from an ordinary distilling flask containing HCl as strong as 50 per cent of the reagent, only requiring to be washed out by repeated additions of acid.

Pentavalent As requires first to be dissolved, second to be treated with a reducing agent in presence of hot concentrated HCl. This also can be done in any kind of distilling flask.

Getting Arsenic into Soluble Form.—Alloys cannot be treated with HCl on account of the formation of arsine. Weigh from 0.5 to ten grams of the alloy sample into a round-bottomed distilling flask of 250 cc. capacity or slightly more. Add just enough water and HNO_3 to dissolve the sample or to oxidize it completely. If much Cu is present, H_2SO_4 may be added at the start. With Sn or Pb predominant, it is better to start with HNO_3 and water. When the alloy is completely decomposed, add H_2SO_2 enough to keep it liquid during fuming. For small samples 5 cc. is enough. For two to five grams 10 cc. will do. For ten grams 20 cc. must be used.

Set the flask in an evaporating can (Fig. 12) on a hot plate and drive off most of the water and HNO_3 . Add a square inch of paper, hold the flask in wooden tongs (Fig. 8) over a flame and blow out the remaining HNO_3 . Heating the acid to boiling and blowing a jet of air into the flask for a few seconds for three times is enough. There should be enough paper added to leave a black residue, which makes it certain that all the HNO_3 is out of the acid at the bottom of the flask. The blowing is depended on to clear the sides and neck.

The use of paper or other organic matter has the other advantages that it helps to reduce the As. The writer absorbed the idea from an unknown source.

Ores, if they contain only acid soluble As, may be treated in the same way as alloy, or by Low's method.¹⁶ If there is a chance that the As is not entirely soluble in acid, as in oxidized Sn or Sb compounds or minerals, the sample should be fused with Na_2O_2 . This is best done in a porcelain crucible, to avoid any suspicion of reduction by flakes of metal afterward. Use as little

¹⁶ Low. "Technical Method of Ore Analysis."

of the flux as possible, leach it out with the least amount of water, wash it into the distilling flask, concentrate some by boiling if necessary, add HCl and boil again, finally obtaining about 50 cc. of 50 per cent HCl. Much SiO_2 will separate, but this does not interfere with the distillation.

Having the As in soluble form in the flask free from HNO_3 , add a large excess of anhydrous FeSO_4 if H_2SO_4 has been used. If the substance is oxidized and soluble in HCl, such as lead arsenate, Cu_2Cl_2 should be used. Five grams of the FeSO_4 or two grams of Cu_2Cl_2 are generally enough. Wash down the neck of the flask with a little water. This will help to prevent bumping. If the sample contains Se or Te, the addition of HCl to concentrated H_2SO_4 will volatilize them, contaminating the distillate. The water precipitates them, after which they are not volatile.

Connect the flask with the condenser, which dips into about 100 cc. of cold water in a beaker, pour in 75 cc. of HCl through the funnel, and simmer gently for about an hour, afterward raising the heat to distil most of the acid more rapidly. Make two additions of 25 cc. each of HCl, boiling down to about 25 cc. after each. The secret of success is to have the sample dissolved with the reducing agent in hot concentrated HCl. Fig. 16 shows the apparatus used in the laboratory of Ledoux & Co.

If the As is trivalent in the sample, or if it is desired to distinguish between trivalent and pentavalent As, the same amount of HCl is added directly to the sample in the flask, without reducing agents, and the distillation conducted rapidly. For samples high in As a Bunsen valve, such as is shown in Fig. 5, with the tip drawn to a tapering point and fitted with a ferule of rubber tubing, is set in the neck of the funnel, so that air may enter during the pulsations of the distillation, but vapors from inside cannot escape. Such a valve will last a long time if it is well washed after each use.

The distilling apparatus is fitted with "sulfree" rubber stoppers, which keep their shape better than the ordinary kind, last longer, and do not distil H_2S when first heated with HCl.

On account of the H_2SO_4 and salts present, there is always a possibility of distilling a little Sb with the As. For this reason,

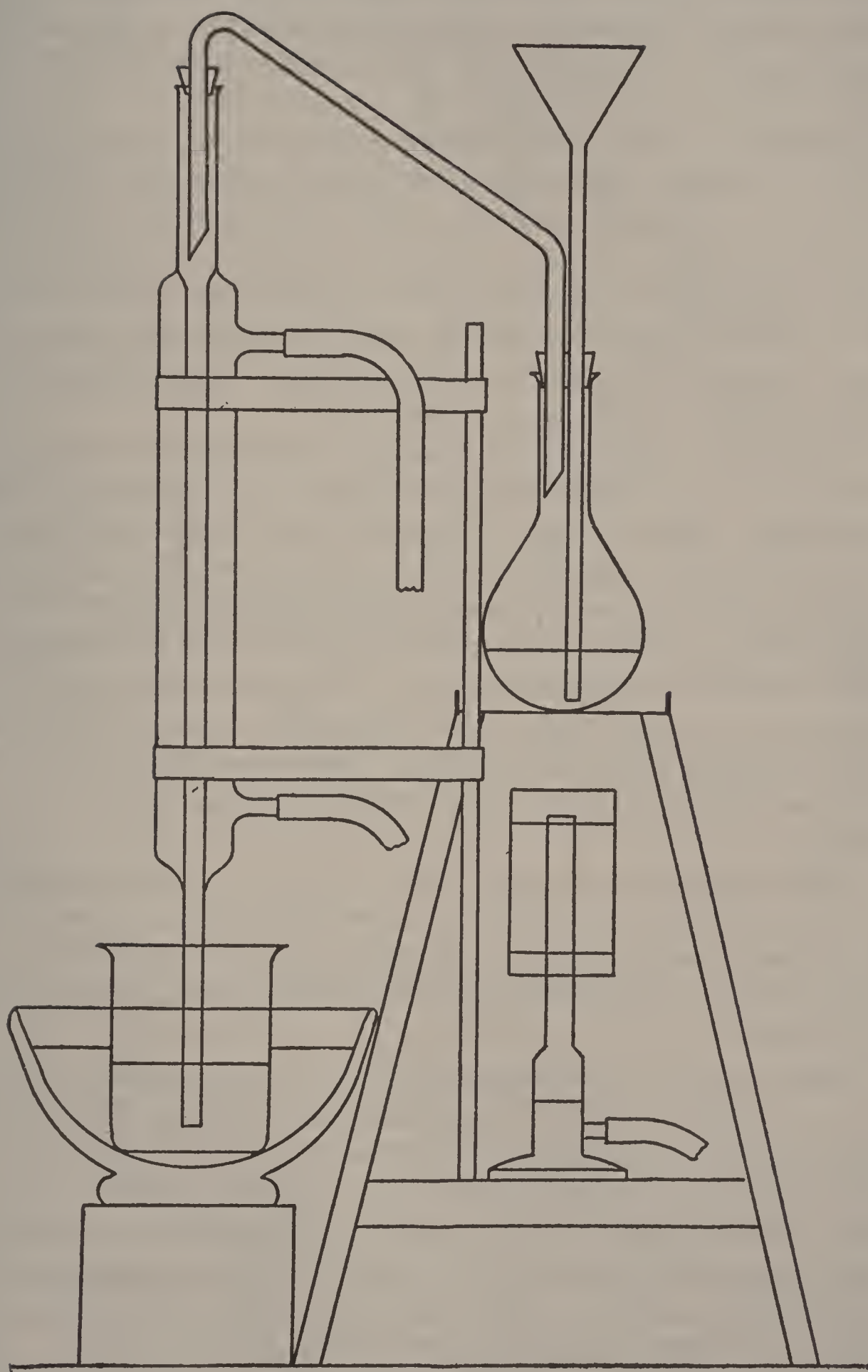


Fig. 16.

when reducing agents have been used and the percentage of As is low enough, it is better to weigh it than to titrate it. By making sure that there is 60 per cent or more of HCl in the distillate, As can be separated from Sb by H_2S .

Antimony in Ores.—While most of the Sb in ores is in the form of stibnite, weathering often produces more or less oxide, which is not soluble in acid. As there is danger of loss when the residue insoluble in acid is ignited preparatory to fusing, it is safer and simpler to fuse all samples at the start. It is possible to save the insoluble by filtering it on the apparatus shown in Fig. 6, drying the residue instead of igniting it before fusion, but for ordinary ores this is too much work.

Use an iron crucible of 75 cc. capacity and weigh into it enough of the ore to contain something less than 0.3 gram of Sb. Add about eight grams of Na_2O_2 , mix well with a smooth spatula and fuse thoroughly. (page 84) Leach in a 400 cc. crucible, add 60 cc. of HCl quickly to prevent precipitation of SiO_2 in a neutral solution, and heat on the water-bath until all iron scales are dissolved. There should be a clear solution. If SiO_2 separates it will be necessary to make a fresh start, using more water to leach the melt and more acid added quickly. This never occurs in a rich ore, and need not occur in any sample weighing less than two grams.

When the solution is clear, dilute it to 300 cc. with hot water and pass a brisk stream of H_2S . Sb particularly needs the extra gas pressure and agitation produced by a rapid stream of the gas, though it may be passed to saturation slowly, and increased only at the end.

Filter and wash with 1 per cent HCl. It is particularly necessary in case of large Sb precipitates to wash by decantation (page 73), as there is much Fe in the solution. If the color of the solution and the precipitate shows that there is little or no Cu, wash the precipitate back and clear the paper by pouring a little stock alkali (page 64) through it, and give it a good washing with hot water. If more than a few milligrams of Cu are present, it will be necessary to treat the entire precipitate. To make sure that there is no Sb lost, unless the amount is very small

treat the residue with H_2SO_4 and HNO_3 to destroy the paper, take up with water and about 10 per cent of HCl to prevent the precipitation of Pb , and repeat the separation. Evaporate the combined alkaline solutions if necessary to 75 cc., and to the warm solution add an excess of KClO_3 and 50 cc. of HCl . Stir until all sulfides are decomposed, as shown by the pale color of the residual S , boil down to 75 cc., reduce as directed on page 112 and titrate.

Separation of Small Amounts of Lead and Iron from Large Amounts of Tin.—The sample should be in HCl solution with the Sn all stannic. Saturate some NH_4OH with H_2S , 10 cc. per gram of the sample, or more if the sample is small. Add NH_4OH in excess to the solution containing the sample and stir in the NH_4SH quickly. After stirring and settling the solution should show clear yellow. If it does not, add more NH_4SH , which may not have been thoroughly saturated. After settling, filter and wash with NH_4SH , keeping the upper edge of the paper wet with washing solution during the filtration to prevent the hardening of SnS_2 , return paper and precipitate to the beaker, boil with dilute HNO_3 , then add H_2SO_4 and destroy the paper, and precipitate the Pb as usual. On dilution, if the PbSO_4 appears clean, separate it. If not, add HCl enough to clear the solution, dilute until the HCl is not more than 2 per cent of the volume, pass H_2S , filter, treat the precipitate with stock alkali, and separate the Pb as usual from the residue.

If the PbSO_4 is clean after the first separation, the Fe will be found in the H_2SO_4 filtrate, but H_2S must be passed to separate a small amount of Sn before Fe can be separated. The Fe obtained in the filtrate should be titrated. Cu , if present in small amounts, can be separated from the H_2S precipitate.

Separation of Small Amounts of Lead and Iron from Large Amounts of Antimony.—If the NH_4SH separation described above does not work well, take a fresh sample, add tartaric acid to the HCl solution and NH_4OH in excess, which will form no precipitate if enough tartaric acid is added. At least 2 molecules of the acid to an H equivalent of the metal are necessary. Pass H_2S , or, for traces, add a measured amount of H_2S water, which

will precipitate Fe, Pb, Bi, and Cu. Filter, dissolve the precipitate and destroy the paper, and proceed as above, separating the elements by the direct scheme. As much Cu can be obtained by this method as by any other, as it is soluble only in polysulfide, which is not formed unless H_2S is in excess.

Separation of Copper from Much Tin and Antimony.—Concentrate the HCl solution by evaporation to a syrup, add tartaric acid in excess over the Sn and Sb, then KOH in excess, which will form no precipitate. Add an excess, or, preferably, KSH formed by saturating KOH with H_2S . Warm until the precipitate settles, filter and wash with hot water or with hot stock alkali. Dissolve the precipitate and fume off the paper with H_2SO_4 , separate the PbSO_4 if it is clean, or dissolve it in HCl and make the regular H_2S separation.

Copper in Ores.—The possibility of acid insoluble Cu in ores is generally disregarded.

Weigh one or two grams of the ore into a beaker, add 20 cc. of water and 10 cc. of HNO_3 , warm and concentrate until the sulfides are decomposed. Add 10 cc. of H_2SO_4 , put a hook under the cover and slowly expel the HNO_3 , finally heating to copious fumes of SO_3 . Cool, dilute, add just enough dilute NaCl solution to precipitate the Ag, dilute, boil and filter. If the ore contains no impurities which will interfere with the clean separation of Cu, add from 5 to 7 cc. of HNO_3 and electrolyse.

Sulfocyanate Separation.—This method is used to separate Cu from elements which interfere with the electrolysis, and is successful for almost every kind of material. It is possible to begin with a solution containing a few cc. of HNO_3 , though a sulfuric or hydrochloric solution is preferable. Ordinarily the solution used is that which would otherwise have HNO_3 added to it for the electrolysis; either an aliquot from bar copper dissolved in H_2SO_4 with a minimum of HNO_3 , the Ag having been separated during the solution; or the H_2SO_4 filtrate from an ore, the HNO_3 having been expelled and the AgCl precipitated before filtering. The solution should be hot or warm.

Add NH_4OH to the solution until a precipitate forms, carefully dissolve it with as little HCl as possible, add about 10 cc.

of 20 per cent NaHSO_3 , stir, and if there is a large amount of Fe which seems not to be reduced, add more. Then add 5 cc. of 5 per cent KCNS solution and stir well. If it is in excess over the Cu, it will give a red color with the still unreduced Fe. If no red, but a large white precipitate appears, add 5 cc. more of the precipitant, as the Cu is still in excess. The red should disappear on standing warm for a few minutes, but its appearance is the best indication that the KCNS is in excess. After the solution has become almost or quite colorless through the reduction of Fe, filter with pulp or on double papers, the outer paper being a size smaller than the inner, wash out the beaker and the top of the filter once with hot water.

Much washing with water will cause the precipitate to run through. The ignition is depended on to complete the separation. If more washing is desired, it can be done with a solution of $(\text{NH}_4)_2\text{SO}_4$. Do not police the beaker but after the filtration wipe it out with a piece of filter paper. Any little rolls of paper left in the beaker can then be washed into the filter. Transfer the precipitate and papers to a silica crucible and roast carefully to expel all chlorides, and then to char off the paper without flame, with plenty of fresh air. The roasting is the critical part of the operation. It can be done singly over a Bunsen burner, but where quantities of crucibles are to be cared for this is not safe. A specially made muffle, heated by gas, or preferably by electricity, which will give the right conditions when the heat is turned on full, is the most reliable.

After the roasting the small residue of charred paper is burnt off over a Bunsen burner, the full heat being used. There should not be the least sign of green in the flame, as this shows that Cu is lost.

Add 5 cc. of HNO_3 to the ignited residue, or more if the amount of Cu is large, cover the crucible with a small cover glass, warm to dissolve, boil for a minute, transfer to a beaker, add H_2SO_4 and electrolyse. There should be little if any red fumes during solution with HNO_3 . Their appearance is evidence of improper roasting. The method requires attention to every detail for success, but the results are accurate, never high. It

can be easily taught to an assistant by one who has learned the use of his apparatus.

Lead in Ores and Waste Materials.—Unless the presence of interfering impurities is known, direct H_2SO_4 treatment is first tried. Weigh one gram of the material into a 400 cc. beaker, add 20 cc. of water and 10 cc. of HNO_3 , warm and concentrate until sulfides are decomposed. In the case of red lead or other material containing peroxides, a reducing agent such as alcohol is necessary. Add 10 cc. of H_2SO_4 and boil down to fumes of SO_3 . Take up with 80 cc. of water, boil, and if the residue appears to be free from gummy or milky adhesions and shows the characteristic dead white finely granular appearance of PbSO_4 , proceed with the conversion of PbCrO_4 . (Page 116).

If the residue insoluble in ammonium acetate is transparent quartz or some other known material which contains no Pb, it may be disregarded and the separation considered complete.

INTERFERING ELEMENTS IN THE LEAD ASSAY

Bismuth.—In the above separation Bi, if present, may cause an error without showing any insoluble precipitate. Part of it will dissolve completely in dilute H_2SO_4 and the rest will go with the Pb, giving a high result. In case of doubt a qualitative test for Bi should be made before precipitating the Pb as PbCrO_4 . Add NH_4OH to the acetate solution. Pb will remain in solution and Bi will precipitate. Filter at once, as Pb is precipitated slowly. Wash the filter with hot water, return it to the beaker, add 5 or 10 cc. of H_2SO_4 , destroy the paper and repeat the separation. In most cases the separation will be complete on the second precipitation. There will be a balance of errors, some Pb being lost in the extra fuming to counterbalance the trace of Bi that may be left. Where the highest accuracy is desired, a check assay on a known amount of Pb and Bi will indicate the necessary correction.

Antimony in the Lead Assay.—When Pb and Sb are evaporated to fumes together, as much as 0.005 gram of Sb will remain in solution and cause no error. A compound insoluble in acetate may be decomposed by fuming off the paper and repeating the

separation. When the amount of Sb is known to be near the limit of separability, as in the case of impure lead bullion, filtering the PbSO_4 , returning it to the beaker and fuming off the paper may be enough.

A residue which is insoluble in ammonium acetate, but which is filterable, should be ignited carefully, fused in sulfur and soda, leached, filtered, washed with NH_4SH , and paper and precipitate boiled with dilute HNO_3 and then fumed with H_2SO_4 , the acetate solution being combined with the main portion. When the acetate is obtained in two portions it is best to divide the 5 cc. of acetic acid used for washing between them, so that there may not be too much in the precipitation of the chromate.

A milky residue may remain which runs through the filter, interferes with the acetate separation, and leaves the assay in doubt. When this is encountered in the course of a long analysis, it is best to stop the filtration, return paper and precipitate to the beaker, fume off the paper, take up with HCl and resort to the H_2S separation. When it occurs in a lead assay, the best thing to do is to start again, by fusing the entire sample with sulfur and soda.

Tin in the Lead Assay.—If a small white precipitate forms in the dilute H_2SO_4 which is known to be Sn and not Sb, as in the analysis of pig tin, it may be ignored. It does not hold lead or interfere with the chromate precipitation.

Calcium in the Lead Assay.—A small amount of Ca will remain in solution in dilute H_2SO_4 and will not interfere. CaSO_4 crystals are easily recognized, as they are large and transparent. If they are seen, proceed with the solution in acetate, but instead of precipitating with chromate, pass H_2S , which precipitates only Pb, filter and convert the sulfide to sulfate. The Ca may be completely recovered in the two filtrates.

Barium in the Lead Assay.—Many pigments contain lead and barium compounds loosely mixed. From these Pb can be completely separated by boiling with HCl , the Ba remaining insoluble and Pb dissolving in the hot moderately dilute acid. From the HCl solution Pb is precipitated with H_2S and recovered as chromate.

If Ba and Pb are evaporated to fumes together a mixed residue insoluble in acetate is formed. The sulfur and soda fusion will not completely decompose it. After the acetate treatment, ignite the residue carefully in a nickel crucible. Fuse with mixed Na_2CO_3 and K_2CO_3 . Leach with water, police and remove the crucible. Add a little NaSH to precipitate any Pb that may be in solution, filter and wash with hot water. Wash the precipitate back, add acetic acid to decompose the carbonates, treating the paper also, pass H_2S just long enough to precipitate the Pb, and filter. Most of the Ba will remain in the filtrate. Recover the Pb from the precipitate and add it to the main portion. This separation was worked out in the Navy Laboratory at Washington.

Separation of Lead as Chloride.—The table of solubilities for Pb in different HCl solutions given on page 51 shows that if the solution is boiled down to constant proportion of HCl and two volumes of water added, the solution on cooling will contain the minimum quantity of Pb for the amount of HCl present. The PbCl_2 can be filtered and washed with 5 per cent HCl and diluted indefinitely without any further separation of PbCl_2 . This gives a convenient method for separating the bulk of the Pb from alloys high in Pb.

Lead in Clean Alloys.—Weigh one gram into a 250 cc. beaker. Add 40 cc. of water, 30 cc. of HCl and 3 cc. of HNO_3 . Heat the mixture almost to boiling until the alloy is dissolved, put a hook under the cover and boil down slowly to a volume of about 30 cc. Add double the volume of water, stir and let stand until cold. Filter on a seven centimeter paper, wash with 5 per cent HCl, dissolve the chloride in ammonium acetate and reserve it.

If the sample contains little or no Cu, saturate 25 cc. of 1:1 NH_4OH with H_2S , add NH_4OH in excess to the filtrate from the PbCl_2 and stir in the NH_4SH . After the precipitate has settled filter and wash with NH_4SH . Return the precipitate and paper to the beaker, boil with HNO_3 1:4 until the sulfides are decomposed, add 5 or 10 cc. of H_2SO_4 , fume off the paper, separate the Pb as sulfate, add the acetate solution to the main portion and precipitate as chromate.

The filtrate from the PbSO_4 will contain all the other elements except the tin group. Traces of the tin group will be found in this filtrate, and must be separated by another H_2S separation before electrolysing the Cu.

If the sample contains Cu, ammonium sulfide does not work well. Add tartaric acid to the HCl filtrate, make it alkaline with NaOH and add a slight excess of NaSH. Warm the mixture until the precipitate has settled, filter and wash with hot water, dissolve the residue in H_2SO_4 by fuming off the paper, separate PbSO_4 and the other elements as usual.

Lead in Impure Metallic Mixtures.—Drosses containing particles of metallic lead, or buttons obtained from the fire assay of drosses, in which different alloys are segregated, should be hammered into fine particles or thin sheets. As much as twenty grams can be used. For that amount use an 800 cc. beaker. There are two methods of solution. If nitrates are to be avoided, add about 300 cc. of HCl and heat to about 80° , adding more acid if necessary to keep PbCl_2 in solution, until the evolution of H ceases. Then add KClO_3 a little at a time until Cl is in excess and all metal is dissolved. Boil the solution until PbCl_2 begins to separate. Add two volumes of water, stir, and let stand until cold.

The other method is to make up a mixture of thirty parts HCl, forty parts water, and three parts HNO_3 . Begin with 400 cc. of the mixture and keep some reserve solution hot. Boil and keep up the volume with the reserve until the metal is all dissolved. If there are pieces of dense iron alloy which do not dissolve, they should be removed by decantation, ground fine and treated separately. Put a hook under the cover and boil down slowly until the PbCl_2 begins to separate. Add two volumes of water, stir and allow to cool.

After cooling, filter into a liter flask, wash with 5 per cent HCl, dilute to the mark and take an aliquot for analysis. Dissolve the PbCl_2 in ammonium acetate, filter it into another liter flask and take a similar aliquot. This may be reserved to chromatate when the Pb has been recovered from the main portion. The residue insoluble in acetate may be fused or otherwise treated to recover the values.

BISMUTH SEPARATIONS

Little Bismuth from Much Lead.—Dissolve the alloy in HNO_3 , precipitate and remove Ag, leaving some excess of HCl to combine with Bi, and to the hot solution add NH_4OH until litmus paper shows exact neutrality. Allow the precipitate, which consists of basic bismuth nitrate or chloride and a little basic lead hydrate, to settle, filter and wash with hot water, disregarding the precipitate which forms in the filtrate. Dissolve the precipitate in HNO_3 , evaporate to dryness on the water-bath and precipitate Bi as BiOCl .

Little Bismuth from Much Antimony and Other Elements.—Place 5 grams of the ore or other material, or, if it is a lead alloy, as much as is desired, in a scorifier, add enough test lead to make eighty grams in all, and scorify to a fifteen-gram button. Dissolve this and recover the Bi as above. This method is suitable only for low percentages of Bi, as there is some loss when large amounts of Bi are scorified. Tests should be made to determine the limits of the method for the conditions of the laboratory.

Separation of Much Bismuth from Customary Impurities.—Dissolve the sample in HNO_3 . If there is an insoluble residue, filter it on a Gooch filter with a belljar into a beaker. Dry the residue, transfer it to a crucible and fuse it with Na_2O_2 . Acidulate the solution with HCl, dissolve or filter off the insoluble, and precipitate the two solutions separately with H_2S . Filter on the same filter, treat the precipitate with NH_4SH and wash with the same. Wash back the residue, add 10 cc. of HNO_3 and enough water to make the solution 20 per cent, and boil until the sulfides are decomposed. Filter, wash with hot 5 per cent HNO_3 and boil out the H_2S from the filtrate. Filter again if necessary, on the same filter. Destroy the paper and dissolve the residue in H_2SO_4 , which will separate the remaining Bi from S. Dilute, boil and filter. Precipitate the two solutions separately with $(\text{NH}_4)_2\text{CO}_3$. This is done by adding NH_4OH almost to neutrality, and then adding an excess of powdered carbonate. Boil, let stand to cool, filter, dissolve the precipitate in HNO_3 , evaporate the solution to dryness and precipitate BiOCl .

Separation of Bismuth from Tellurium.—Occasionally a BiOCl precipitate will be colored yellow by Te. In this case, take a fresh sample, make the ordinary H_2S precipitation to get rid of Fe, treat with NH_4SH if there appears to be much of the Sn group, wash back the BiS , boil with dilute HNO_3 to dissolve it, filter and reserve the residue. Boil out H_2S from the filtrate, add tartaric acid and add NH_4OH in excess, which should form no precipitate. Pass H_2S , which will precipitate Bi free from Te. The precipitate may be filtered on the filter containing the previous insoluble residue, washed with NH_4SH , and Bi recovered as before.

Separation of Cadmium from Much Zinc.—Dissolve the sample in 20 per cent H_2SO_4 , adding a few drops of HNO_3 from time to time if necessary to hasten the solution, but taking care not to leave more than 1 cc. excess at the end. This applies, of course, only to metal, which will decompose HNO_3 . If the sample is spelter, take from ten to twenty-five grams and use 0.85 cc. of acid per gram, with addition of 10 to 15 cc. for final excess. When all zinc is dissolved, disregarding the small insoluble residue which may be mostly Pb, add ten to fifteen grams of $(\text{NH}_4)_2\text{SO}_4$, dilute to an acidity of less than 5 per cent and pass H_2S . In the absence of ammonium salts a little Cd may escape precipitation. Let the solution stand to settle, pass H_2S again and filter. Wash a few times with water. Save the filtrate for Fe, if that is to be determined.

Return the paper to the beaker, add 10 cc. of H_2SO_4 , destroy the paper with HNO_3 and separate the PbSO_4 . Dilute the filtrate to 4 per cent acidity, add five grams of $(\text{NH}_4)_2\text{SO}_4$, repeat the precipitation, and filter. Add the filtrate to the previous one for total Fe.

If there is a chance of the Sn group being present, treat the precipitate with fresh NH_4SH to avoid loss of Cu, fume off the paper again and repeat the H_2S separation, using 5 cc. of H_2SO_4 . Test the filtrate, which should be almost or entirely free from Zn. If much Zn shows, some may still be in the precipitate. If necessary, repeat the separation. The $\text{Cd} + \text{Cu}$ may be determined by electrolysis as directed on page 121. To determine

Cd as CdSO_4 , add NH_4OH in excess to the H_2SO_4 solution, then NaCN solution until the blue of Cu is destroyed, and a little more, and precipitate CdS . Dissolve the sulfide in H_2SO_4 by destroying the paper and make the determination as directed on page 122.

Separation of Small Amounts of Copper and Antimony from Much Tin.—Dissolve ten grams of the alloy in a mixture of 25 cc. of water, 50 cc. of HCl , and 10 cc. of HNO_3 , in an 800 cc. beaker. The action will become violent suddenly at the end of the solution. Boil to make sure of complete oxidation, remove the cover and evaporate on the water-bath to small bulk. Dilute to 200 cc., add concentrated KOH solution in excess, then twenty-two grams of oxalic acid and ten grams of ammonium oxalate, dilute at once to 600 cc., stir well and heat until all is in solution. Pass H_2S in a vigorous stream to saturation, or pass it slowly for fifteen minutes, heat the solution again, and give a rapid stream for one minute. Filter, wash slightly with water, treat the residue with KOH and filter into a 400 cc. beaker. If the bases did not dissolve entirely in oxalic acid on account of the low solubility of the oxalates of copper and lead, it may be necessary to fume off the paper, take up with HCl , add ammonium oxalate, which will free some oxalic acid, and repeat the separation. If there is much Sb, in any event it will be necessary to get some of it out of the filtrate from the PbSO_4 . There will then be two alkaline solutions containing Sb, which may be combined, evaporated to 75 cc., and determine Sb as directed on page 112.

The Cu will be found in the final residue after separating the last trace of Sb by stock alkali. Some Pb will be in the oxalic acid filtrate with Sn, so that it is better to make the lead determination on a separate portion by NH_4SH .

As a small amount of Cu is dissolved by the stock alkali, the result will be slightly low. The Cu can be recovered by oxidizing the alkaline sulfide solution with Na_2O_2 (page 129). The Cu is precipitated as oxide after the sulfides are decomposed. There is a possibility of some sodium antimonate being precipitated also, but this will not occur unless much Sb is present. It would

be an advantage to have K_2O_2 for this separation, to make sure of keeping Sb in solution.

Analysis of the Metastannic Acid Precipitate.—This is obtained in the analysis of bronze and solder. There are several schemes described for precipitating it, but none of them are perfect. In any case there will be a trace of Sn in solution, and the precipitate is never pure. If concentrated HNO_3 or fuming HNO_3 is used on a sample containing S there will be some $PbSO_4$ formed. It is better, therefore, to use slightly dilute acid. The precipitate will contain part of the As, all of the Sb if it is not more than a quarter as much as the Sn, some of the Cu, about 0.15 per cent in a normal bronze, a large part of the Fe, all of the P, some of the Mn, and possibly some Pb.

For ordinary bronze, weigh three grams into a 250 cc. beaker. For solder use 0.5 gram. Add 25 cc. of water and 15 cc. of HNO_3 . Warm until action ceases, boil until red fumes are gone, dilute to 100 cc., and allow the precipitate to settle. If it stands over night filtration is easier.

Set a rapid nine-centimeter filter with pulp, filter and transfer the precipitate to the filter with cold water. Wash once with hot 10 per cent HNO_3 and then several times with hot water.

Put the precipitate into a weighed porcelain crucible, roast off the paper carefully and burn off all carbon. Put the crucible in a muffle and heat uncovered for five minutes at a temperature high enough to soften porcelain slightly. Then cover and heat for fifteen minutes if the temperature is more uniform when the crucible is covered; otherwise one heating for fifteen to twenty minutes will do. Heating to a high temperature covered without preliminary oxidation causes loss. The muffle may be made for use with a blast lamp as follows:

Take two Denver thirty-gram crucibles, knock out the bottoms so as to leave holes about one inch in diameter, support one of them in a ring over the blast lamp and fit a triangle into the middle of it. This can be done by fitting a ring of heavy iron wire into the crucible and laying a legless triangle on it, or the legs of a triangle may be bent down to fit the sides of the crucible. Platinum is best. Nichrome will last a long time. Make a cone of

molded asbestos, with a base no larger than the top of the crucible to be heated, set it in the triangle, dry it and burn out the carbon. Invert the other Denver crucible on top of the first for a chimney, set the blast lamp vertically under and adjust the flame to give the proper heat. The full heat of a good blast lamp is too much. The flame should be oxidizing, and long enough to surround the asbestos cone. Porcelain sticks less to asbestos when hot than it does to another piece of porcelain.

After the muffle is hot, put in the crucible uncovered, heat for five minutes, cover and heat for fifteen minutes. When the ignition is properly made, the precipitate is of a uniform color and does not stick to the bottom of the crucible. Cool in a dessicator and weigh. Constant weight should be obtained at the first heating, but in starting to use a muffle one should make sure by repeated heating of a sample.

After weighing add from two to five grams of sulfur and soda mixture (page 85) and fuse. It is not necessary to mix the sample, and the crucible can be heated at once to fusion temperature for fifteen minutes.

Leach, filter on an ashless nine-centimeter paper, wash thoroughly with NH_4SH , reserve the filtrate and ignite the residue. Weigh the residue, treat it in the crucible with a little HCl until Cu and Fe are dissolved, dilute, filter, ignite the residue and weigh. The difference between these residues measures the oxides of Fe , Cu , Pb , etc. They may be determined separately, or the HCl filtrate can be evaporated with a little H_2SO_4 taken up with water and the solution filtered on the same filter with the main portion for the determination of Pb and Cu . A little Fe and a considerable amount of Al will be added to the sample from the crucible, so that this portion cannot be used for them.

The alkaline filtrate from the sulfur and soda fusion contains all of the Sb in an ordinary bronze, and some of the As . If the Sb is more than one-eighth as much as the Sn , this method should not be trusted for it, but it will have to be determined on this portion as well, in order to correct the Sn determination. The same is true of the As . The solution will also contain the P . This is generally determined on a separate portion, but it can

be taken from this. If it is necessary to do so, acidulate the solution with HCl, filter, add 0.2 gram of Fe to the filtrate, in the form of a ferric salt, precipitate the Fe, and determine P as in the analysis of steel. The sulfide precipitate should be dissolved in stock alkali.

To the alkaline solution containing the Sn, Sb, and As, add an excess of KClO_3 and HCl with stirring until the sulfides are decomposed. No heat should be applied and just enough acid added to decompose the chlorate slowly. Then add enough HCl to decompose the rest of the KClO_3 , boil out the Cl and concentrate the solution to give half strength HCl, filter the solution on an asbestos filter (page 14) and wash with an equal volume of concentrated HCl, pass H_2S and precipitate As_2S_5 , filter on a weighed Gooch crucible and wash with 60 per cent HCl, then once with water, dry and weigh as As_2S_5 . Concentrate the filtrate to 75 cc. and determine Sb by the bromate method.

Calculate P to P_2O_5 , As to As_2O_5 , and Sb to Sb_2O_3 , add the oxides already determined and deduct the sum from the ignited tin precipitate. The difference is SnO_2 . If this method is carried out carefully it is the most accurate known for the complete analysis of bronze. It has the advantage that the major elements are all determined on the same portion, so that the footing will show whether the results are accurate in the frequent cases where duplicates disagree owing to unevenness in the sample. The remaining solutions are available for the determination of all the other elements except Fe and Al. It may be noted that Ti is also introduced into the solution from the porcelain crucible fusion.

Volumetric Tin from the Metastannic Acid Precipitate.—When Sn is determined in bronze, it is often necessary to determine also Cu, Pb, and Zn, but not Sb or As. For this purpose the volumetric method is easier than the gravimetric.

Obtain the metastannic acid precipitate as in the gravimetric method, transfer it to an iron crucible, ignite, mix well with five to eight grams of Na_2O_2 and fuse. Leach with water, add 65 cc. of HCl, keep the solution hot until all iron scales have dissolved,

transfer the solution to a flask, reduce with nickel and titrate with iodine. (Page 113).

Lead, Copper, Zinc and Nickel in Bronze.—Proceed as in the gravimetric analysis, evaporate the filtrate from the metastannic acid to about 50 cc., add 10 cc. of H_2SO_4 (page 75) evaporate to fumes, take up, boil, and cool.

Instead of weighing the residue insoluble after the sulfur and soda fusion, destroy the paper with acid, using 5 cc. of H_2SO_4 . Dilute this, boil and cool. Filter the two H_2SO_4 solutions through the same filter, using the smaller as a washing for the larger, into an electrolysis beaker, add 7 cc. of HNO_3 , and electrolyse. If the apparatus available will not accommodate the quantities here described, the whole determination can be done on a smaller scale, using one or two grams of the sample.

Dissolve the PbSO_4 and convert it to chromate.

In taking down the electrodes, it is better to allow a little Cu to dissolve than to lose any of the solution or to dilute it much. The best way is to plug out the current, drop the beaker, put another under the electrodes and wash them with a wash-bottle. Then they can be rinsed in more water and dried with alcohol or acetone. The electrolysis beaker is emptied into the one used for the first rinsing, which having a lip is more convenient for filtering.

Pass H_2S into the cold solution. The precipitate will contain what Cu was lost from the electrode, and some Sn. This is partly from the fused SnO_2 , and cannot be used as a correction on the volumetric Sn. Ignite the precipitate, dissolve out the Cu with HNO_3 , take it up with water and NH_4OH and determine Cu by color. (Page 120).

Boil the H_2S out of the filtrate, add NH_4OH and $(\text{NH}_4)_2\text{S}_2\text{O}_8$, precipitate Fe, Al, and Mn and filter. Wash with the solution used for Zn in ores. The precipitate may be used for Mn and Fe, but will give slightly high results for Fe.

Neutralize the filtrate with HCl and make it just acid. If the acid is added drop by drop with stirring until a piece of litmus paper is seen to change from purple to dull red, and then

with another drop to bright red, the conditions are right for the separation.¹⁷

Pass H_2S for 15 minutes and let the solution stand cold until it settles, or over night. Filter on an eleven-centimeter paper with pulp, and wash beaker and paper once with cold water, filling the filter. Return the paper and precipitate to the beaker, add 10 cc. of water, 7 cc. of HCl , dissolve the ZnS , add ten grams of NH_4Cl , dilute and titrate by Low's method.¹⁸

Add HCl to the filtrate, boil out the H_2S and precipitate the Ni as glyoxime.

Iron and Aluminium in Bronze.—Weigh five grams into an electrolysis beaker, add 25 cc. of water, 10 cc. of H_2SO_4 , and, cautiously, 10 cc. of HNO_3 . Put the beaker on a cold or warm stove and gradually increase the heat, boil out red flames, dilute and electrolyse. Transfer the electrolyte to an ordinary beaker, add 10 cc. of HCl , boil until the solution is clear, dilute and separate Sn by H_2S , boil out and oxidize the solution and precipitate Fe and Al together with NH_4OH . Wash the precipitate with NH_4Cl solution to remove Zn , and then wash both beaker and precipitate thoroughly with hot water to remove chlorides. If the precipitate is large it is best to dissolve it in H_2SO_4 and reprecipitate to make sure that nitrates are removed. Dissolve the precipitate with 10 cc. of 20 per cent H_2SO_4 , pass the solution through the reductor, preferably a small one, and titrate the Fe .

Precipitate Fe and Al in the solution after titration by the basic acetate method, bringing the solution to exact neutrality by dilute NH_4OH and adding no extra acetic acid but only a gram of acetate, to make sure that all Al is precipitated. Filter and wash slightly.

Stopper the lower end of the funnel with a rubber plug made by boring a stopper, and sharpened on an emery wheel. Make up a hot 20 per cent H_2SO_4 solution, measure out 2 cc. and pour it drop by drop around the top of the filter, stirring with the rod until the precipitate dissolves. Now remove the plug and let the solution run into the beaker. Before washing the filter use

¹⁷ Treadwell. "Quantitative Analysis." Scott. "Standard Methods."

¹⁸ Low. "Ore Analysis."

the filtrate to dissolve all of the precipitate that remains on the sides of the beaker. Wash into the electrolytic apparatus with a mercury cathode and electrolyse to remove Fe.¹⁹

The rotating anode is unnecessary in the use of the mercury cathode, if time enough is given, and as it is not to be weighed, the apparatus is easily made. An ordinary tumbler with a hole bored in the side at the bottom, a wire introduced through a rubber plug, and enough mercury inside to cover the wire, makes the cell and the cathode. The anode is made of a platinum wire bent into a horizontal coil with the riser at the side, so that a cover glass with a notch in the side will cover the beaker. The volume of the solution should be about 100 cc. and the current from one-tenth to one ampere.

Fe does not dissolve out of the mercury in the very dilute acid when the current is stopped, so that no special device is necessary for quick disconnection. The solution is filtered away from the mercury, by decantation as much as possible. Add 10 cc. of HCl to the filtrate, neutralize with NH_4OH , boil, and let the solution stand to settle. A trace may not show itself at once.

If the sample contains P, it will be found with the Al as AlPO_4 . If it is in excess over the Al the precipitate may be assumed to be of that composition. It may be advisable to precipitate all the Al as AlPO_4 by the addition of more phosphate before the neutralization, but generally the quantity is so small that it makes little difference how it is weighed. All that is needed is to know that it is below a certain percentage.

SEPARATION OF THE ALUMINIUM GROUP

After the H_2S group has been separated, the solution must be oxidized in such a way as to leave nothing that will precipitate MnO_2 in an alkaline solution. Peroxides and persulfates cannot be used for this purpose, as they do not boil out of an acid solution. Aqua regia will do. If either HNO_3 or HCl is already in the solution enough of the other acid may be added. There should be at least 2 cc. of HNO_3 and 8 cc. of HCl to make sure of oxidizing the Fe in an ordinary ore analysis, and

¹⁹ Smith. "Electro-Analysis."

the solution should be boiled for a few minutes. It is best to boil out all the H_2S and have a clear solution before making the oxidation, or S will precipitate.

As the ordinary ore contains both Fe and Al, and as Cr is comparatively rare, the basic acetate separation adapted to Al is most commonly used.

Basic Acetate Precipitation.—This has already been described on page 104, in the way that it should be used in quantitative analysis. Before neutralizing, the solution should be concentrated to 100 cc. or less and should be cold, as this makes it easier to get the neutral condition.

As the washing of this precipitate is difficult, it is easier to dissolve it in HCl or H_2SO_4 and repeat the separation than to try to wash out all of the unprecipitated elements. There may also be some occlusion which washing will not break up. Reprecipitation should be practiced whenever the Ni or Co color is visible, and when the amount of Ca is large enough to give a brisk evolution of CO_2 when the fresh sample is treated with HCl . The filtrates should be evaporated during the subsequent precipitations, so that they can eventually be combined in one beaker.

After the basic acetate separation, the precipitate is dissolved in dilute H_2SO_4 . Dilute it to about half the final volume used for the basic acetate separation, put in a piece of litmus paper and add NH_4OH until the solution is barely alkaline. Boil and smell the steam. When the odor of NH_3 is barely perceptible the solution is neutral. Remove it from the heat, add the pulp of an ashless filter large enough to hold the precipitate, stir it in and let it settle. Filter and wash well with hot water. Combine all the filtrates, add NH_4OH in slight excess, and boil them down to about 400 cc. If any $\text{Al}(\text{OH})_3$ separates, filter it, wash it well with hot water, and add it to the main precipitate.

If the main precipitate cannot be rubbed out of the beaker completely, use a piece of ashless paper moistened with 1 per cent H_2SO_4 . This will loosen without dissolving it. Place the wet precipitate and paper in a weighed porcelain or platinum crucible. Silica should not be used, as it cracks after the bisulfate fusion.

Roast off the paper and ignite uncovered with the crucible slanting and the flame at the back, so that fresh air can reach the precipitate. After the carbon is all burned off, apply the blast lamp, using an oxidizing flame, with the crucible first uncovered and then covered, so as to dehydrate the Al as much as possible and reduce the Fe as little as possible. Weigh and repeat the ignition to constant weight. The effect of the paper pulp is to leave the ignited residue fine and flaky, easily dehydrated and easily fusible, instead of being in hard lumps as it otherwise would be. The ignited precipitate consists of Al_2O_3 , Fe_2O_3 , TiO_2 , and P_2O_5 . Fuse it with bisulfate as described on page 81. After leaching the fusion, if there is an insoluble residue, filter, ignite and fuse it in a small amount of bisulfate. If it still does not dissolve, make other tests to find out what it is.

Pour the clear solution through the reductor and titrate it with KMnO_4 . Add a drop of H_2O_2 if the reagent is free from P, or else use Na_2O_2 , and determine Ti by color comparison with a standard solution.²⁰ As much as 0.005 gram of TiO_2 may be disregarded so far as its effect on the Fe titration is concerned, but it must be counted in the analysis of the precipitate. If there is a larger amount of Ti, the determination of Fe must be modified.

The Fe is first reduced by H_2S and titrated. (Page 122.) Then the reductor is equipped with a tube leading to the bottom of the flask and enough ferric sulfate solution put in to give a proportionately large excess over the Ti, with enough solution for the end of the tube to dip two or three centimeters under the surface. The density of the solution must be decidedly less than that containing the sample, so that the latter will stay under.

The sample should contain about 10 per cent of free H_2SO_4 , so that it will evolve H freely in contact with the Zn. Start the reductor with some 10 per cent acid to clear all the air out of it and replace it with H. Then pass the sample in slowly, so that it will take about ten minutes to go through. Follow with 10 per cent acid and then water, so that the Ti shall be in an atmosphere of H until it has been mixed with the ferric solu-

²⁰ Low. "Ore Analysis."

tion. Ti will reduce its equivalent of Fe, which does not oxidize so quickly in the air, so that the titration is conducted in the same way as for Fe alone.

Before titrating, see that the Ti solution has been well mixed with the other. The H may do it, but it is well to make sure. The titration figure, less that obtained for the H_2S reduction, gives that for Ti.²¹

Phosphates.—If the special Ti titration has been made, it is as well to depend on a separate P determination. If not, some time may be saved by getting the P from the solution after titrating. Make a rough basic acetate precipitation to separate the Mn, dissolve the precipitate in 18 cc. of HNO_3 , filter it into a 400 cc. beaker, add 15 cc. of NH_4OH , dilute to 150 cc. and at a temperature of 40 to 50° add 40 cc. of ammonium molybdate.²²

Stir occasionally for ten minutes and let stand for an hour. Filter on a weighed Gooch crucible and wash with 2 per cent HNO_3 . Dry at 100° if the precipitate is small, or at 110° if it is large. The weight times 1.63 equals P.²³ By subtraction the weight of Al_2O_3 is found.

Separation of Uranium from Interfering Elements.—All U minerals are soluble in acids. As the H_2SO_4 solution is preferable later, start with HNO_3 and expel it with as little H_2SO_4 as will give a liquid excess, not more than 5 cc. Enough of the sample should be taken to contain about 0.25 gram, unless the percentage is very low. Five grams is the ordinary amount for commercial ores.

Destroy organic matter if the material contains it, by repeated additions of HNO_3 , finally expelling all HNO_3 . Take up with water, pass H_2S and filter. Boil out H_2S .

Add Na_2O_2 to the cold filtrate to oxidize Fe and V. Then add Na_2CO_3 a little at a time with stirring until the solution is alkaline and there is a gram or two of undissolved carbonate. Add a little Na_2O_2 from time to time during the neutralization to keep the V red, if it is present.

Boil the solution for fifteen minutes, add ten grams of $(\text{NH}_4)_2\text{SO}_4$, allow the solution to cool somewhat and filter. The sodium

²¹ Gooch. "Methods in Chemical Analysis."

²² Blair. Scott.

²³ Blair, "The Chemical Analysis of Iron."

carbonate treatment is the best way to precipitate Fe, and the conversion later to the ammonium salt helps to precipitate Al. The precipitation of Al is not complete, and should not be. Dissolve the precipitate and repeat the precipitation. If the second filtrate shows a yellow color, make a third separation. Combine the filtrates, add H_2SO_4 in excess, and about five grams of $(\text{NH}_4)_2\text{HPO}_4$ and boil out the CO_2 . Add to the hot solution, which should be about 400 cc., slightly dilute NH_4OH in excess. Then add acetic acid until litmus paper shows red, not more than 1 cc. excess. When cool, filter with pulp.

U by itself makes a difficult precipitate to filter, but the presence of a little Al coagulates it and makes filtration easier. Wash the precipitate with a cold solution of ammonium sulfate and acetate, slightly acid.

In the neutral solution, U and V are precipitated together, but if a phosphate is present in excess in the acid solution the U prefers it and leaves the V in solution. Under these conditions, however, V is only slightly soluble, and may form dense orange crystals which dissolve slowly in the washing solution.

Dissolve the precipitate in hot dilute H_2SO_4 and test for V with H_2O_2 . If there is the slightest trace, the precipitation must be repeated. Add two grams of the phosphate, dilute with hot water, and add ammonia and acetic acid as before.

After V is separated, dissolve with 10 cc. of H_2SO_4 , filter into a 400 cc. beaker, and evaporate to fumes. At the first appearance of fumes remove the beaker and add small particles of KMnO_4 in excess to destroy organic matter. Take up with water, pass the solution through the reductor under the same conditions as are suitable for Fe, shake the flask for one minute, and titrate. The accurate determination of the end correction in this determination is important.

Separation of Much U from Little Impurities.—Use a large weight, five to ten grams. Dissolve in HNO_3 , pass H_2S , filter, boil out H_2S , add $(\text{NH}_4)_2\text{CO}_3$ in excess, so as to dissolve all U, and then a little NH_4SH . Let the solution stand until the precipitate settles, preferably over night. Filter and wash with the same reagents. Repeat the separation if it appears to be neces-

sary. Acidulate the filtrate, boil out H_2S , take an aliquot which contains about .25 gram of U_3O_8 , add 5 cc. of H_2SO_4 and NH_4OH in excess. Warm until the precipitate settles and filter with pulp. Wash with hot $(\text{NH}_4)_2\text{SO}_4$ solution, ignite in a porcelain crucible, using the full heat of the Bunsen flame, and weigh.

Dissolve the residue in the crucible with a little HNO_3 . Filter if there is an insoluble residue of SiO_2 and weigh the residue. Keep the volume of the filtrate down as much as possible. Add $(\text{NH}_4)_2\text{CO}_3$ in slight excess, warm slightly, and if a precipitate collects, filter and weigh it as Al_2O_3 . Acidulate and concentrate the filtrate and test with H_2O_2 for V. If any appears, determine it by comparison with a standard solution of V. Calculate it to V_2O_5 . Deduct the impurities, and report the difference as U_3O_8 .

INDEX

	PAGE
Acetic acid, reagent	69
Alloy dissolving mixture	77, 91
Alkali stock solution	64, 98
Alloys, decomposition of	75-78, 91, 93
Aluminium, properties	54
— identification	106
— determination	123, 152
— dissolving	78
— group separations	105, 150
— in bronze	149
Ammonia water, reagent	63
Ammonium acetate solution	92
— salts, reagent	63
Antimony, properties	46
— identification	103
— determination	111
— in bronze	138
— in ores	134
— from Pb and Fe	135
— little, from much Sn	144
Apparatus	6
Aqua regia	76
Arsenic, properties	45
— identification	97, 98, 102
— determination	110, 111
— separations	130-134
Asbestos filters	14
— choice of	15
Balance, chemical	25
Barium, properties	61
— identification	95, 108
— in Pb assay	139
Basic acetate separation	104, 151
Beaker tongs	19
Bismuth, properties	52
— identification	100
— determination	118
— in Pb assay	138
— little, from much Pb	142
— little, from much Sb	142

	PAGE
Bismuth (Continued)	
— from usual impurities	142
— from Te	143
— water precipitation	101
Bisulfate fusion	81
Boron, properties	41
Bromine, properties	44
— and bromides, reagent	68
Bronze, separation of Pb, Cu, Ni and Zn	148
— separation of Fe, Al and P	149
Burettes, calibration and use	27
 Cadmium, properties	 53
Cadmium identification	101
— determination	121
— from much Zn	143
Calcium, properties	60
— identification	108
— determination	127
— in Pb assay	139
Calculations, tabulation method	34
— geometrical	39
Calibration of glassware	27, 33
Carbon, properties	41
Chlorates, reagent	68
Chlorides, reagent	67
Chlorine, properties	44
Chromium, properties	55
— identification	107
— determination	124
Cobalt, properties	59
— identification	108
— determination	127
— from Ni	108
Copper, properties	52
— identification	101
— determination	119-121
— in bronze	148
— in ores	136
— from much Sn and Sb	136
— little, from much Sn	144
— sulfocyanate separation	136
Correction for scale	40
Crucible lifter	18
Cyanides, reagent	70

	PAGE
Decantation, washing by	73
Decomposition of alloys	75
— of alloys and salts	91
— of ores	78, 93
— of slags and silicates	79
Evaporating in flasks	23
Evaporation of solutions	75
Filter rack	6
Filtering	72
Filters, setting	12
— choice of	12
— paper	72
— reinforced	14
— asbestos, in funnel	14
Flask cover for evaporation	23
— tongs	19
Flasks, calibration of	29
Fluorine, properties	44
Funnels, shape of	12
Fusion methods	81-86
— mixture	83
Glass, old, making fusible	1
Glass-working	1-6
Gooch crucible	14
— crucible holders	16
Hydriodic acid, reagent	69
Hydrochloric acid, reagent	67, 75
Hydrofluoric acid, reagent	66
Hydrogen, properties	41
— sulfide generator	9
— sulfide precipitation	95
— sulfide test	97
Hydrosulfuric acid, reagent	69
Iodides, reagent	69
Iodine, properties	45
Insoluble residues, treatment of	80, 94
Iron, properties	57
— identification	105
— determination	122
— in bronze	149
— little, from much Sb	135
— little, from much Sn	135

	PAGE
Lead, properties	51
— identification	100
— determination	115-118
— in alloys	140
— in impure metallic mixtures	141
— in bronze	148
— in ores and waste materials	138
— little, from much Sb	135
— little, from much Sn	135
— separation as PbCl_2	140
— separations	138, 139
— chloride, separation	76, 91
— chloride, solubility	51
Lithium, properties	62
— identification	109
Magnesium, properties	60
— identification	108
Manganese, properties	58
— identification	107
Marking glazed surfaces	15, 21
Mercury, properties	50
— identification	99
Metastannic acid precipitate, analysis	145
— acid precipitate volumetric Sn in	147
Molybdenum, properties	49
— identification	97
— determination	97
— from Sn, Sb, As, Se and Te	102
Mouthpiece	23
Nickel, properties	59
— identification	108
— determination	127
— from Co	108
— in bronze	148
Niter and soda fusion	83
Nitric acid, reagent	65, 77
Nitrogen, properties	41
Ores, acid decomposition	78, 79, 93
— fusion methods	81, 86
Organic matter, destroying by acid	74
Oxalic acid and oxalates, reagent	70
Oxides, dissolving	79, 93
Oxidizing mixtures	77
Oxygen, properties	41

INDEX

161

	PAGE
Paper pulp	12, 13
Pencils for glass and porcelain	15, 21
Phosphorus, properties	43
— identification	106
— determination in Al precipitates	153
Pipette, dipping	24
Pipettes, calibration and use	28
Policemen	21
Potassium, properties	61
— identification	109
— bromate titration	113
— salts, reagent	64
Pouring bottle	22
Precipitation	71, 74
Properties of elements	41
Pulp, paper, use of	12, 13
Qualitative analysis	87-109
Reprecipitation	74
Residue, insoluble	80, 94
Rubber stoppers	20
— tipped rods	21
Selenium, properties	48
— from Te	103
Silicates, dissolving by acid	79
Silicon, properties	42
Silver, properties	50
— identification	100
Slags, decomposition	79
Sodium, properties	61
— identification	109
— carbonate fusion	82
— hydroxide fusion	86
— peroxide fusion	84, 94
— salts, reagent	64
— stannite, reagent	100
Stock alkali solution	64, 98
Strontium, properties	61
— identification	108, 95
Sulfides, reagent	69
— decomposition of	78, 93
Sulfur, properties	42
— and soda fusion	85
Sulfuric acid, reagent	64, 78

	PAGE
Tabulation method for direct ratios	34
Tartaric acid, reagent	69
Tellurium, properties	49
— from Se	103
Tin, properties	47
— identification	103
— determination	103, 113
— from Fe and Pb	135
— in lead assay	139
— oxide, ignition	145
— separations	129, 136
— volumetric, from metastannic acid precipitate,	147
Titanium, properties	57
— identification	106
— determination	152
Tongs for beakers and flasks	19
Tungsten, properties	43
— identification	93, 94
Uranium, properties	55
— identification	107
— determination	125
— separations	153
Vanadium, properties	56
— identification	106, 107
— determination	124
Volumetric apparatus calibration table	29
Wash bottles	9
Washing precipitates	72, 73
Water overflow system	9
Weights, adjusting	26
Zinc, properties	59
— identification	108
— determination	125
— from Ni and Co	107
— in bronze	148

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
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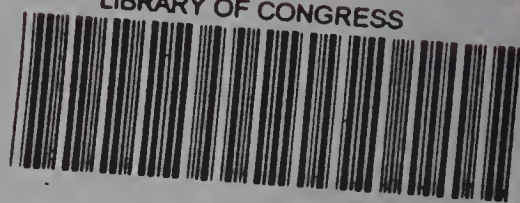
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